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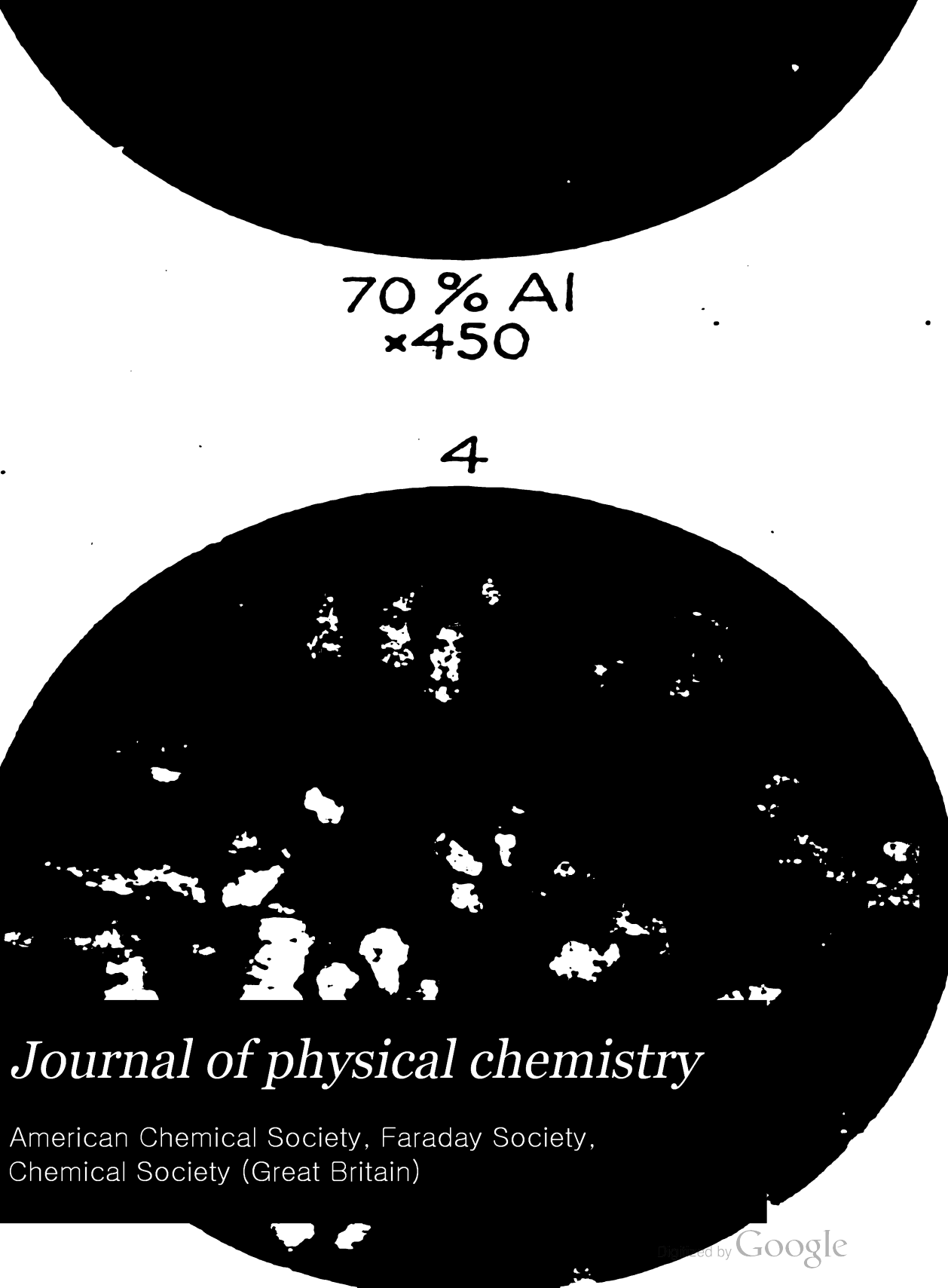
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# THE JOURNAL OF PHYSICAL CHEMISTRY

EDITED BY  
WILDER D. BANCROFT      JOSEPH E. TREVOR

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## THE TOXIC ACTION OF ACIDS AND SALTS ON SEEDLINGS<sup>1</sup>

BY F. K. CAMERON AND J. F. BREAZEALE

Activity in the investigation of the action of solutions of various electrolytes on living organisms has been pronounced within the past few years, stimulated largely by the fact that the hypothesis of electrolytic dissociation has seemed to offer a guiding principle in this work. The interest of the chemist in this line of investigation has been especially augmented by the well-known work of Kahlenberg<sup>2</sup> and his associates, from which it has been concluded that while some of the observed phenomena support, nevertheless the weight of the evidence is against the validity of the hypothesis of electrolytic dissociation, at least in the form which it is now generally understood. Perhaps the most important work in this line of investigation, from the point of view of dissociation studies, has been that involving the action of solutions of acids, the action of the hydrogen ion being relatively so large in comparison with other ions that it has been supposed the effect of the latter might safely be disregarded as of vanishing importance when the former was present. Similar assumptions have sometimes been made regarding the action of the hydroxyl ion as compared with the other ions. But it has been repeatedly demonstrated that when comparing the action of other dissociation products of electrolytes the effect of both cation, anion and the undissociated electrolyte must be considered.

In the course of an investigation being carried on in this

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<sup>1</sup> Published by permission of the Secretary of Agriculture.

<sup>2</sup> Kahlenberg and True. *Bot. Gaz.* 22, 81 (1896); Heald. *Ibid.* 22, 125 (1896); True. *Am. Jour. Sci.* (4) 9, 183 (1900); Kahlenberg and Austin. *Jour. Phys. Chem.* 4, 553 (1900); Kahlenberg and Mehl. *Ibid.* 5, 113 (1901); Kahlenberg. *Ibid.* 5, 339 (1901). For a more extended bibliography, see Report 71, U. S. Department of Agriculture, 1902, pp. 56-60.

laboratory, the death or "toxic" limit of concentration in aqueous solution of a number of acids and the corresponding potassium and calcium salts, as well as mixtures, were carefully determined for certain plant seedlings. It is believed that this work has sufficient interest as a contribution to the study of the dissociation hypothesis to justify publication from that point of view, although the work was undertaken with quite a different purpose.

In work of this character great difficulty has been encountered in deciding what criteria should be taken as determining the death of the plant. The concentration required to kill a seedling or disorganize an entire radicle varies widely from that required to completely hinder any growth or elongation, or that which will permit some elongation but will kill the root tip and of course ultimately produce death. All these criteria have been used by various investigators, so that a comparison of their results is often exceedingly difficult if not impossible.<sup>1</sup> To illustrate this point the following table is presented, showing a comparison of the relative concentrations required to kill the entire wheat seedling and to just permit life without injuring the tip of the radicle.

TABLE I.

Solute	Toxic limits for	
	Whole seedling	Tip of radical
Sulphuric acid	N/9	N/15000
Hydrochloric acid	N/10	N/18000
Nitric acid	N/7	N/15000
Acetic acid	N/13	N/20000
Oxalic acid	N	N/15000
Succinic acid	N	N/20000
Calcium chloride	N/3	N/4
Calcium nitrate	N/3	N/5

The criterion which apparently has found the most favor

<sup>1</sup> For instance, the figures given in this paper for wheat are in no way comparable to those which have already been obtained by Coupin, since the manipulation and criteria used were so widely different.

and which has been used in former studies in this laboratory,<sup>1</sup> was the obvious death and flaccid condition of the tip of the radicle for the first 15 millimeters from the apex. But in some of the experiments with solutions of potassium salts, the apices of the radicles instead of becoming flaccid when the toxic limit was reached, became excessively hard, brittle and transparent.<sup>2</sup> The determination of the toxic limit was much more difficult in these cases, requiring nice judgment and much experience. But while the results obtained with potash salts may possibly lack the accuracy of those obtained with acids or lime salts, owing to the necessary use of criteria which are far from being sharp and decisive, yet they are believed to be sufficiently near the truth to justify the use of them in the argument of this paper.

Generally, before the death of the extreme 15 millimeters the radicle had somewhat elongated from plumule to the apex. These death criteria usually became apparent within 24 hours and definite results were practically always obtainable after this interval of time. Frequently, however, the experiments were prolonged for a week or more. In these latter cases there was often a development of new roots. But whenever these new roots penetrated the solution the death phenomena were observed in their tips, so that it seems perfectly safe to say that the concentration of solution producing death of the tip of the radicle would ultimately prove prohibitory to the growth of the plant, and, therefore, that safe and reliable criteria were used.

Solutions insufficient in concentration to prohibit growth might however seriously retard it. It was generally observed that the radicles immersed in solutions of a concentration approaching the death limit tended to curl up in an apparent effort to leave the solution, seeking a more congenial environment. This curving of the radicles away from the injurious solution was noticed in the former studies<sup>3</sup> in this laboratory upon the white lupine and alfalfa. It is also noteworthy that

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<sup>1</sup> Report 71, U. S. Department of Agriculture, 1902.

<sup>2</sup> Similar observations were made by Heald (*loc. cit.*) when working with salts of nickel, cobalt, etc.

<sup>3</sup> Report 71, U. S. Department of Agriculture, 1902.

the stimulating effects of concentrations much below the toxic limits frequently observed and discussed by other investigators was especially marked in solutions of acids.

It was further observed that the absolute length of the radicle from plumule to apex, if the seedlings did not vary too much in age, appeared to have no effect upon the result, death occurring in equal strengths of solution within 24 hours, no matter what length of radicle was immersed in the solution when first introduced or at the end of 24 hours.

It has been found in all investigations of this character that the amount of sunlight accessible to the seedling during the experiments has a marked effect upon the strength of the solution which they can withstand. The experiments here recorded were conducted in a room to which there was no access of direct sunlight, and in which the illumination was quite feeble, though sufficient to enable one to conduct this work readily. The experiments were all made in the late winter so that the illumination probably exerted a very feeble effect, though the conditions were not strictly comparable with those obtaining in a dark closet. Check experiments carried on in the dark showed that in some instances the seedlings would stand slightly higher concentration than the results herein given. But the differences were small and always insufficient to justify abandoning the advantage of watching the development of the plants from time to time, which was secured by working in a feebly lighted room. These differences were only of a noticeable character with wheat, barely observable with clover, and practically did not exist with corn.

In almost every experiment made there were found to be individual idiosyncrasies of the seedlings, some being very much less affected than others and surviving in concentration sufficient to kill the majority. The figures given here represent the concentrations just permitting growth to continue in upwards of 60 percent of the seedlings in from 3 to 8 duplicate experiments, each experiment involving 4 seedlings of corn, 6 to 8 of wheat, or 8 to 10 of clover. In narrowing down the limits

between which these duplicates were made, from 20 to 30 experiments were required.

A practically constant temperature of about 25° C was maintained in the room where the experiments were conducted.

The seedlings were sprouted in a specially prepared box between new blotting papers, moistened with distilled water. They were kept at a temperature of about 25° until the primary radicle had reached the desired length and then removed from the germinating box and transferred as quickly as possible to the vessels containing the solution.

These vessels were cylindrical vials about 9 centimeters high and 4 centimeters in diameter. They were repeatedly washed before being used, and it seems improbable that the solubility of the glass could have affected the results. Attempts to prevent any such solution by coating the interior of the vial with paraffine, etc., were found unsatisfactory and, as tested by a few check experiments, probably unnecessary.

The seedlings were picked up as tenderly as possible, the radicle inserted through a loop in a platinum wire and the plants let down into the solution until the greater part of the radicle was immersed. The platinum wire passed through a tight-fitting cork with a small slit in it to allow ventilation. This furnished a support for the plants and allowed freedom of movement up or down, so that a desired immersion of the radicle could be readily obtained. The vials under observation were placed under glass bell-jars in which there was a small open vessel containing distilled water. A separate vial in which the radicles were immersed in distilled water was carried along with each set as a check.

The plants used in this investigation were wheat (*Triticum vulgare*), Indian corn (*Zea mays*), clover (*Trifolium pratense*), cowpeas (*Vigna catjang* \* \* ), cotton (*Gossypium herbaceum*), and white lupine (*Lupinus albus*). With the cowpeas and cotton it was found impossible to obtain satisfactory results under the conditions described, no matter what concentrations were used, and they will not, consequently, be given here. The work

with the white lupine was only preliminary in character and was done for the purpose of acquiring experience in manipulation, and to test whether the procedure and criteria used would furnish results in satisfactory agreement with those formerly obtained by Kahlenberg and True, and in the previous work of this laboratory.

With wheat, 594 experiments were made, about 2600 seedlings being used. The small size of the seedlings of this plant made the work quite difficult. The radicles moreover are normally, nearly transparent or translucent, so that the effect of the solution was often uncertain. With clover, 688 experiments were made with about 5000 seedlings. These were even more difficult to handle than the wheat, not only on account of their size, but also because of their extreme sensitiveness to the action of the dissolved electrolytes. With corn, 550 experiments were made, using about 2500 seedlings. This proved to be a very satisfactory plant for this kind of work, the only difficulty encountered being the tendency for a mold to appear quickly and accumulate in the vials in which the seedlings of this plant were being tested.

The large number of experiments cited were occasioned by the fact that we have attempted to work within narrower limits than has hitherto been attempted. In the case of corn in solutions of acids the results given are within 0.00001 N of the strength of solutions on either side of that determined as representing the toxic limit. With wheat and clover the absolute value of the probable experimental error is even smaller, though considered on a percentage basis this might not be so.

The solutes used were carefully examined to secure purity, in many cases the substances being prepared by ourselves. Great care was exercised in making up the various concentrations and duplicate preparations were made, to guard against errors as far as possible, since no analytical methods of sufficient delicacy were available to check this work.

The results obtained in solutions containing a single solute are given in Table II. They are stated in terms of the dilution,

that is, the number of liters containing one gram equivalent of the solute.

TABLE II.

Toxic Limits for Seedlings in Solutions of Single Solutes

Name of solute	Toxic limits for		
	Corn	Wheat	Clover
Hydrogen sulphate	3000	15000	20000
" potassium sulphate	3000	—	—
" chloride	3000	18000	20000
" nitrate	2250	15000	20000
" acetate	850	20000	20000
" oxalate	1750	15000	20000
" succinate	600	20000	20000
" malate	1250	20000	20000
Potassium sulphate	22.5	12.5	55
" chloride	15	12.5	12.5
" nitrate	25	15	30
" acetate	12.5	*	*
" oxalate	25	15	90
" succinate	20	*	*
" malate	10	*	*
" carbonate	85	95	140
Calcium chloride	4	4	5
" nitrate	4	5	5
" acetate	9	*	*

The results obtained with corn are generally in very good accord with those published by Heald<sup>1</sup> as the result of his work with this plant. But Heald worked between limits of concentration far wider than we employed, and in consequence we have felt justified in stating our results in detail. Heald found that

<sup>1</sup> Loc. cit. In his tabulation of results, Heald gives the toxic limit for acetic acid as N/400, but from the description of his experiments it would appear that it should be N/800. Loew (Science, 18, 304 (1903)) gives the toxic limit for sulphuric and hydrochloric acids as N/512, although no reason is apparent for this wide discrepancy from the results of Heald and those presented here. See also Science, 18, 411 (1903).



corn seedlings would just survive in the same relative strength of nitric acid as of sulphuric or hydrochloric acid, namely, N/3200, while we found by repeated experiments that the seedlings would survive in much stronger solutions of nitric than of the two other acids. In fact an N/3000 solution, which in the case of sulphuric or hydrochloric acid would barely permit growth, was in the case of nitric acid by no means sufficient to seriously retard growth.<sup>1</sup>

In the case of clover the uniformity of the figures for the limits in acid solutions is very striking. It might be supposed that this uniformity was only apparent owing to the difficulties inherent to work with such a sensitive organism and with such highly dilute solutions. But great care was exercised in determining these limits, and it was conclusively shown that an N/17500 solution of any of these acids would kill or absolutely inhibit the growth of upwards of 60 percent of clover seedlings. The figures obtained for wheat were determined within as narrow limits as those for clover.

The spaces (\*) in the table under the columns for wheat and clover are occasioned by the fact that it was impossible to prepare the solutes with a purity sufficient to obtain satisfactory results. A very slight excess of base or acid would totally invalidate the results owing to the extreme sensitiveness of wheat or clover to these solutes. It was found to be practically impossible to prepare solutions of the salts indicated which would neither be alkaline nor contain free acid sufficient to make an N/20,000 solution with respect to it.

In saturated solutions of the slightly soluble sulphate, oxalate, succinate, malate or carbonate of calcium, seedlings of corn, wheat or clover all thrive vigorously.

In distilled water nearly saturated with respect to carbon dioxide, it was found that a large majority of corn seedlings sur-

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<sup>1</sup> Kahlenberg and Mehl, loc. cit., working with young bass, found decided differences in the toxic effect of equivalent solutions of these acids.

vived, but that seedlings of wheat<sup>1</sup> or clover were invariably and quickly killed. In the work formerly done in this laboratory it was found that dissolved carbon dioxide had no effect upon seedlings of white lupine other than a slightly stimulating one. Whatever value these results may have for other studies, they can not be considered to have any for the mooted question as to the actual existence of carbonic acid and its dissociation in aqueous solution.

The results obtained with clover seedlings in acids would indicate that the toxic action was due to the hydrogen ion alone; for it must be assumed that with a dilution N/20,000 practically complete dissociation existed for each and every one of the acids. But the results obtained with the wheat seedlings are not in harmony with this view, since the dilutions here were also such as to insure practically complete dissociation, although quite different concentration of the several acids gave the toxic limit. Curiously enough, from this point of view, acetic, succinic, and malic acids were found to be more toxic than sulphuric, hydrochloric or nitric acids, although the former are weaker acids than the latter.

With the corn seedlings in acid solution the results are quite as difficult to interpret. They cannot be regarded as due to the effect of the hydrogen ion alone, as the concentration with respect to this substance in the solutions representing the toxic limits varies considerably. The approximate amount in grams of hydrogen as ion in some of these solutions are as follows: <sup>2</sup>

<sup>1</sup> This is in apparent opposition to the observation of Jentys, *Bull. Internat. Acad. Sci. Cracovie*, 1892, 306 (1893), that wheat in a pot was practically unharmed by the passage of carbon dioxide through the soil. But it should be borne in mind that seedlings or plants which have received even serious injuries may make a fair growth when the cause of the injury is removed, as by the subsequent aeration of the pot through which the carbon dioxide had been passed. In illustration of this survival of injuries it might be cited that seedlings of wheat, the roots of which had been allowed to stand 24 hours in a N/10 solution of sulphuric or nitric acid, and thus very badly damaged, when transferred to distilled water, a nutrient solution, or soil, frequently thrive, sending out new roots in place of those which had been destroyed.

<sup>2</sup> Computed from conductivity measurements, *Physikalisch-Chemische Tabellen*, Landolt and Börnstein, 2 Aufl., pp. 496-501 (1894).

TABLE III.  
Corresponding Concentrations with Respect to Acids and Ionized Hydrogen

Solute	Dilution	Grams H-ion per 100,000 liters solution
Sulphuric acid	N/3000	33
Hydrochloric acid	N/3000	33
Nitric acid	N/2250	44
Acetic acid	N/850	13
Succinic acid	N/600	26
Malic acid	N/1250	40

Assuming, as has generally been done in previous work of this kind, that the action of the sulphuric and hydrochloric acid solutions were entirely due to the hydrogen ions, it would be necessary to assume that the acetic and succinic acids, the anions or the undissociated solute or both had also a similar toxic effect which was not of a negligible magnitude; but that with nitric and malic acids, the anions and undissociated solutes had a retarding or ameliorating effect. The necessity of such assumption would seem to absolutely invalidate the use of such organisms and criteria as we have been considering for the testing of the dissociation hypothesis in any quantitative way.

In considering the figures in Table II obtained for the potassium salts, difficulties are encountered quite as serious. If the toxic effects are to be ascribed mainly or alone to the ions present, it is not easy to see why clover seedlings should be able to withstand a twelfth-normal solution of potassium chloride, while a thirtieth-normal potassium nitrate or a fiftieth-normal potassium sulphate solution marks the limit. And in the case of the wheat seedlings it is no more explicable why they should be able to stand a more concentrated solution of the sulphate and chloride than of the nitrate or oxalate, which latter, if anything, are the less dissociated. Without citing further details, a casual inspection of the figures obtained in the corn seedlings would show them to be quite as confusing.

It does not seem possible to consider these results as pro-

duced mainly by the cations and modified by the anions, in view of the results obtained with the wheat seedlings, where, for instance, nitric acid was found to be less toxic than hydrochloric or sulphuric acid, but potassium nitrate to be more toxic than the corresponding potassium salts of the other acids just mentioned. Moreover, with the clover seedlings all the acids possessed the same relative toxicity, while the potassium salts varied very widely.

The results obtained with lime salts, while interesting as compared with those obtained with the corresponding potassium and hydrogen compounds, do not seem to throw any additional light upon the value of this method for studying dissociation phenomena and need no further discussion here.

In Tables IV and V are given results obtained in solutions of acids when in addition to the free acid the indicated amounts of a corresponding potassium or calcium salt, respectively, were also present.

TABLE IV.

Death Limits for Seedlings in Solutions of Acids Containing Various Amounts of the Corresponding Potassium Salts

Name of plant	Name of solute	Toxic limits with respect to free acid in solutions containing		
		0 Potassium	N/100 Potassium	N/50 Potassium
Corn	Sulphuric acid	3000	2100	1750
	Hydrochloric acid	3000	2500	1750
	Nitric "	2250	2100	1750
	Acetic "	850	700	500
	Oxalic "	1750	1000	800
	Succinic "	600	75	60
Wheat	Malic "	1250	750	125
	Sulphuric "	15000	8000	7000
	Hydrochloric "	18000	8250	7250
	Nitric "	15000	7750	7000

We are not in possession of sufficient information to determine the effect of these several salts upon the dissociation of the

acids. But it seems very improbable that if the data were at command, it could assist in explaining the wide variations in the effect of calcium in ameliorating the toxic effect of acids upon corn seedlings; or why potassium should be less effective in reducing the action of hydrochloric than that of sulphuric or nitric acid, when the radicles of wheat seedlings are immersed in the solution. And even less could we thus look for an explanation of the fact that the presence of potassium salts apparently increases the toxic effect of acids upon seedlings of clover.

TABLE V.  
Death Limits for Seedlings in Solutions of Acids Containing Various Amounts of Corresponding Calcium Salts

Name of plant	Name of solute	Toxic limits with respect to free acid in solutions containing			
		0 Calcium	N/100 Calcium	N/50 Calcium	Saturated with calcium
Corn	Sulphuric acid	3000	950	700	400
	Hydrochloric acid	3000	1750	1200	—
	Nitric “	2250	1500	1000	—
	Acetic “	850	500	400	—
	Oxalic “	1750	—	—	1500
	Succinic “	600	35	20	10
	Malic “	1250	200	100	100
Wheat	Sulphuric “	15000	3250	2250	—
	Hydrochloric “	18000	3250	2750	—
	Nitric “	15000	3000	2000	—
Clover	Sulphuric “	20000	3250	1750	1700
	Hydrochloric “	20000	4000	2750	—
	Nitric “	20000	3500	1750	—
	Oxalic “	20000	—	—	15000

This last statement is not shown in the table because of the uncertainty in determining accurately the concentration of a solution so dilute as were those involved. It seemed wiser, therefore, to simply state the results of the experiments in general terms rather than give questionable figures. This is of

special interest as being, so far as we are aware, the first instance observed when the addition of a second electrolyte to a solution of another, has not reduced the toxic action.

The value of such studies as the one here recorded in throwing light upon physiological questions, explaining the rationale of such practical problems as the art of fertilizing, liming of soils, etc., is probably great. But the uncertainties and difficulties attendant upon them and which have been brought out in this paper, the impossibility of ignoring the physiological peculiarities and idiosyncrasies<sup>1</sup> of the organisms, and the nature of the consequent results make it evident that they have little or no value for a quantitative investigation of dissociation phenomena. In so far as the dissociation hypothesis aids in the explanation of the observed phenomena, that fact is itself in favor of the validity of the hypothesis. Its failure to meet all cases<sup>2</sup> does not mean necessarily that the hypothesis is incorrect, but that other factors must be considered. Finally it seems safe to conclude that the method we have been considering can not be expected to furnish definite information as to the existence of ionic dissociation in aqueous solution. And the arguments based upon similar work, which have been advanced hitherto, must now be regarded as doubtful in value if not entirely inadmissible.

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<sup>1</sup> That plants exercise a selective absorption of their mineral nutrients from solution, and that this inherent power is only modified, but not necessarily obliterated by the presence of undesirable substances or undesirable amounts of otherwise desirable substances, is generally admitted. That this power may be exercised toward "ions" has already been suggested, Report 71, U. S. Department of Agriculture, p. 68, and may explain some of the difficulties encountered in this work. But as the suggestion has so far failed to indicate specific conclusions, it has not been considered worth while to discuss it here.

<sup>2</sup> In this connection, Vide Jour. Phys. Chem. 4, 553 (1900), and 5, 339 (1901).

# ON THE DIELECTRIC CONSTANTS OF SOLVENTS AND SOLUTIONS<sup>1</sup>

BY HAROLD EVERETT EGGERS

## INTRODUCTION

The specific inductive capacity of different substances and solutions has not been extensively investigated until recently. Indeed, it was not until 1838 that the existence of such a property was first announced by Faraday,<sup>2</sup> and it was he who first devised a means for the measurement of specific inductive capacities, or dielectric constants.

Faraday's apparatus for this purpose was comparatively simple, consisting merely of two concentric spherical shells insulated from each other, but both accessible to external contact. By first charging the condenser so formed to a given potential difference, the dielectric medium being air, and measuring the quantity of the charge held; and then filling the space between the spheres with the substance to be investigated, and repeating the process, he was able to obtain quantitative results.

Since this time, improved methods for the measurement of dielectric constants have been worked out along several lines. Of these, perhaps the simplest method is that described by Silow,<sup>3</sup> and used, with various modifications, by Tomasnewski,<sup>4</sup> Cohn and Arons,<sup>5</sup> Tereschin,<sup>6</sup> Franke,<sup>7</sup> and others. This method, in its essentials, consists of measuring the variation in deflection

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<sup>1</sup> This paper was prepared as a thesis for the degree of Bachelor of Science at the University of Wisconsin, June, 1903. This thesis was awarded the Science Club Medal as the most meritorious bachelor's thesis in science for the year 1903. It was also awarded special honors by the Faculty of the University of Wisconsin.

<sup>2</sup> Phil. Mag. 13, 412 (1838).

<sup>3</sup> Pogg. Ann. 156, 189 (1875).

<sup>4</sup> Wied. Ann. 33, 33 (1888).

<sup>5</sup> Ibid. 28, 454 (1886). Also 33, 14 (1888).

<sup>6</sup> Ibid. 36, 792 (1889).

<sup>7</sup> Ibid. 50, 163 (1893).

of a system of one or more quadrant electrometers, upon changing the dielectric medium between the needle and the quadrants of the instrument. Another method involving the use of the quadrant electrometer is that of Heerwagen.<sup>1</sup>

A third method, employing the Wheatstone bridge in comparing capacities, has been elaborated in late years by Nernst.<sup>2</sup> As improved and modified by him, it is claimed that this method is fitted for measuring the dielectric constants of very weak electrolytes, as well as of non-conducting liquids.

A fourth type of apparatus is that in which the determinations are made by adjusting a system of variable capacity to positions of resonance for electrical waves. To this class belong the methods of Thwing<sup>3</sup> and of Drude.<sup>4</sup> Results obtained by Thwing, compared with those of other investigators, would seem to leave his method somewhat open to criticism.<sup>5</sup> Those obtained by the methods of Nernst and Drude, however, agree both with each other and with the results of other observers.

In this investigation, which was undertaken at the suggestion of Prof. Kahlenberg, the object was a two-fold one. First, it was desired to continue the work begun in this laboratory by Dr. Schlundt,<sup>6</sup> in measuring the dielectric constants of various hitherto uninvestigated solvents. Second, work was begun on what, so far as the writer can learn, is practically an entirely new field,—the investigation of the dielectric constants of solutions resulting from the combination of various solids with non-conducting liquids.

#### Apparatus

The apparatus employed was similar to that described by Drude in the *Zeitschrift für physikalische Chemie*, Vol. 23, 267 (1897). As the description there given by him is very complete, repetition of it here would be superfluous. Of the two

<sup>1</sup> Wied. Ann. 48, 35 (1893).

<sup>2</sup> Zeit. phys. Chem. 14, 622 (1894).

<sup>3</sup> Phys. Rev. 2, 35 (1894).

<sup>4</sup> Zeit. phys. Chem. 23, 267 (1897).

<sup>5</sup> Ibid. 23, 297 (1897).

<sup>6</sup> Bull. University of Wisconsin, Science Series, 2, 353 (1901).



methods he describes, the second was adopted. This, while not so accurate as the first, permits the use of small quantities of solvent, and further, allows the complete enclosure of the solvent during the determination. This latter feature was particularly desirable with the solvents with which the writer worked, the majority of them being organic sulphur compounds, with indescribably offensive odors.

One slight modification to Drude's apparatus, that advocated by Goodwin and Thompson,<sup>1</sup> was adopted. This consisted of tipping the spark gap terminals with platinum, to insure greater durability.

Three condenser bulbs of different capacities were used. Of these, only the one of least capacity, for use with solvents of high dielectric constants, was similar to those described by Drude. This type is illustrated in Fig. 1. For the others, the types shown in Figs. 2 and 3 were adopted.

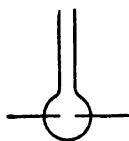


Fig. 1

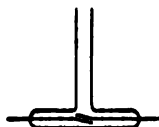


Fig. 2

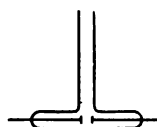


Fig. 3

They were made by fusing platinum terminals into the ends of the branches of a small T-tube. The advantages of this form of bulb are several. The bulbs are easier to construct, and can readily be made of no greater cubical content than the other style. And, farther, they possess the distinct advantage, particularly for the work undertaken here, of being much more readily filled, an important feature when working with malodorous sulphur compounds. The filling was done by means of a slender-tipped, long glass pipette, operated with a rubber ("medicine dropper") bulb.

The liquid used about the spark gaps was ordinary kerosene. It was found necessary to frequently remove and filter this, as it was decomposed to a considerable degree by the electric spark, and the finely divided carbon, which resulted from

<sup>1</sup> *Phys. Rev.* 6, 38 (1899).

the decomposition, interfered with the proper working of the apparatus.

The induction coil used to operate the apparatus was constructed by Ritchie, Brookline, Massachusetts. It required a current of approximately two amperes, about ten volts being impressed across the terminals. The current was furnished by nine to eleven storage cells, an adjustable rheostat in series serving to properly regulate the current. The spark furnished by the coil, in air, was 4 to 6 cm long.

To calibrate the instrument, seventeen liquids, consisting of mixtures of acetone and water, and benzene and acetone, were used. The dielectric constants ranged from 80.9, that of water, to 20.5, for acetone, and 2.26 for benzene. The values for the intervening solutions are given by Drude in his article.

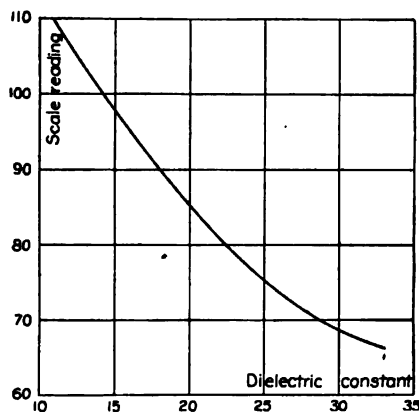


Fig. 4

Calibration curve of condenser bulb

For each bulb, a curve was plotted with dielectric constants as abscissæ, and the corresponding scale readings as ordinates. By referring to the curve so obtained the scale reading for the substance under investigation, its dielectric constant was obtained directly. One of the calibrating curves so obtained is shown in Fig. 4: it is a good example of the nature of the curve, as well as of the range through which the bulb gave accurate results.

For each determination, at least ten settings, and frequently

more, were made. After the scale reading for the liquid of unknown dielectric constant had been found, two additional determinations were made with calibrating solutions having scale readings nearest to that of the substance investigated. In this way any error due to shifting of the zero of the instrument was eliminated.

By taking these precautions, a limit of error of about 3 percent was attained. It was practically impossible to be more accurate than this. Drude states that he found his method accurate to about 1.5 percent; but my experience was confirmed by Dr. Schlundt, who worked in this laboratory with other apparatus of the same type, and he told me that he found that about 3 percent was his limit of error.

The substances used in making up the calibrating solutions were as follows: The benzene was Kahlbaum's thiophene-free product; it was distilled from phosphorus pentoxide, and boiled at 79° under 741.43 mm pressure. The acetone was Schuchardt's chemically pure; it was allowed to stand for twenty-four hours over anhydrous copper sulphate, and on distilling from the copper sulphate its boiling-point was found to be 55.5°, under 738.43 mm pressure. The water used had a specific conductivity of  $5 \times 10^{-6}$  reciprocal ohms.

## PART ONE

### Results

Methyl sulphocyanate,  $\text{CH}_3\text{SCN}$ , Schuchardt's preparation. As it came in a hermetically sealed bottle, and was perfectly colorless, it was not redistilled. The average of two determinations gave 33.3 for its d. c.,<sup>1</sup> at 15.5°

Ethyl sulphocyanate,  $\text{C}_2\text{H}_5\text{SCN}$ , Schuchardt's preparation. Distilled at 142.5°, 738.8 mm pressure. Average of four determinations gave 31.2 for its d. c., at 11.5°.

Amyl sulphocyanate,  $\text{C}_5\text{H}_{11}\text{SCN}$ , Schuchardt's preparation. Distilled at 195°, 740.29 mm pressure. Average of three determinations gave 17.1 for its d. c., at 19.5°.

<sup>1</sup> The abbreviation d. c. is used throughout the presentation of results, for dielectric constant.

Methyl mustard oil,  $\text{CH}_3\text{NCS}$ , Schuchardt's preparation. Was well crystallized, and had a melting-point sharply defined at  $35^\circ$ , so it was not redistilled. Average of three determinations gave 17.9 for its d. c., at  $40^\circ$ .

Ethyl mustard oil,  $\text{C}_2\text{H}_5\text{NCS}$ , Schuchardt's preparation. Distilled at  $131.2^\circ$ , 733.33 mm pressure. Average of three determinations gave 22 for its d. c., at  $15^\circ$ .

Allyl mustard oil,  $\text{C}_3\text{H}_5\text{NCS}$ , Schuchardt's preparation. Distilled at  $150^\circ$ , 737.87 mm. pressure. Average of three determinations gave 17.33 for its d. c., at  $17.6^\circ$ .

Phenyl mustard oil,  $\text{C}_6\text{H}_5\text{NCS}$ , Schuchardt's preparation. Distilled at  $219^\circ$ , 741.32 mm pressure. Average for four determinations gave 8.5 for its d. c., at  $11.6^\circ$ .

Amyl sulph-hydrate,  $\text{C}_5\text{H}_{11}\text{SH}$ , Schuchardt's preparation. Distilled at  $115.5^\circ$ – $116^\circ$ , 739 mm pressure. Its dielectric constant ranged from 4.9, at  $18^\circ$ , to 4.4, at  $26^\circ$ , and 4.25, at  $33^\circ$ . These results agree fairly well with that of Schlundt,<sup>1</sup> who found its d. c. to be 4.35, at  $22^\circ$ .

Phenyl isocyanate,  $\text{C}_6\text{H}_5\text{NCO}$ , Schuchardt's preparation. Distilled at  $162.5^\circ$ , 741.3 mm pressure. Average of these determinations gave 5.56 for its d. c., at  $17^\circ$ .

Thiophene,  $\text{C}_4\text{H}_4\text{S}$ , Schuchardt's preparation. Distilled at  $84^\circ$ , 739.1 mm pressure. Its d. c. was found to be 2.85, at  $13.5^\circ$ , 2.7, at  $32^\circ$ , and 2.55, at  $55^\circ$ . Turner,<sup>2</sup> it was found, had previously measured the dielectric constant of this substance, by Nernst's method; he found it to be 2.76, at  $16^\circ$ .

Ethyl disulphide,  $\text{C}_2\text{H}_4\text{S}_2$ , Schuchardt's preparation. Distilled at  $163^\circ$ – $163.5^\circ$ , 739.14 mm pressure. Average of three determinations gave 15.63 for its d. c., at  $19^\circ$ .

Thioacetic acid,  $\text{CH}_3\text{COSH}$ , Schuchardt's preparation. Distilled at  $95^\circ$ , 734.57 mm pressure. Average of four determinations gave 17.3 for its d. c., at  $21^\circ$ .

Acetyl acetone,  $\text{CH}_3\text{CO.C}_2\text{H}_5\text{CO}$ , Schuchardt's preparation. Distilled at  $136.5^\circ$ – $138^\circ$ , 734.82 mm pressure. Average of three determinations gave 25.67 for its d. c., at  $18^\circ$ . It was

<sup>1</sup> Bull. Univ. of Wis., Science Series, 2, 369 (1901).

<sup>2</sup> Zeit. phys. Chem. 35, 385 (1900).

found after the measurement had been made, that this substance had been previously measured by Drude. He found its d. c. to be 26, at 22°.

Acetyl methyl-hexane ketone,  $\text{CH}_3\text{CO}-\text{C}_7\text{H}_{15}-\text{CO}$ . Schuchardt's preparation. Distilled at 195°–196.5°, 739.14 mm pressure. Average of three determinations gave 27.4 for its d. c., at 19°.

Malonic nitrile,  $\text{CH}_2(\text{CN})_2$ , Schuchardt's preparation. Came well crystallized, so was not farther purified. Melted at 30°. Average of five determinations gave 46.3 for its d. c., at 36.2°.

Pinacolin,  $\text{CH}_3\text{COC}(\text{CH}_3)_3$ , Schuchardt's preparation. Distilled at 104.5°, 754.31 mm pressure. Average of five determinations gave 12.6 for its d. c., at 17.5°.

Nitranisol.  $\text{C}_7\text{H}_7\text{NO}_3$ . Schuchardt's preparation. It was distilled in vacuo, boiling at 138°–140°, 20 mm pressure. Average of five determinations gave 23.8 for its d. c., at 19.8°.

#### DISCUSSION OF RESULTS

For convenience, the results given above are here repeated in tabular form.

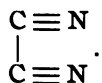
Substance	Formula	Dielectric constant	Temp.
Methyl sulphocyanate	$\text{CH}_3\text{SCN}$	33.3	15.5
Ethyl sulphocyanate	$\text{C}_2\text{H}_5\text{SCN}$	31.2	11.5
Amyl sulphocyanate	$\text{C}_5\text{H}_{11}\text{SCN}$	17.1	19.5
Methyl mustard oil	$\text{CH}_3\text{NCS}$	17.9	40.0
Ethyl mustard oil	$\text{C}_2\text{H}_5\text{NCS}$	22.0	15.0
Allyl mustard oil	$\text{C}_3\text{H}_5\text{NCS}$	17.3	17.6
Phenyl mustard oil	$\text{C}_6\text{H}_5\text{NCS}$	8.5	11.6
Amyl sulph-hydrate	$\text{C}_5\text{H}_{11}\text{SH}$	4.9	18.0
Phenyl isocyanate	$\text{C}_6\text{H}_5\text{NCO}$	3.36	17.0
Thiophene	$\text{C}_4\text{H}_4\text{S}$	2.85	13.0
Ethyl disulphide	$\text{C}_2\text{H}_5\text{S}_2$	15.6	19.0
Thioacetic acid	$\text{CH}_3\text{COSH}$	17.3	21.0
Acetyl acetone	$\text{CH}_3\text{COC}_2\text{H}_5\text{CO}$	25.7	18.0
Acetyl methyl hexyl ketone	$\text{CH}_3\text{COC}_7\text{H}_{15}\text{CO}$	27.4	19.0
Malonic nitrile	$\text{CH}_2(\text{CN})_2$	46.3	32.6
Pinacolin	$\text{CH}_3\text{CO}(\text{CH}_3)_3$	12.6	17.5
Nitranisol	$\text{C}_7\text{H}_7\text{NO}_3$	23.8	19.8

<sup>1</sup> Zeit. phys. Chem. 23, 311 (1897).

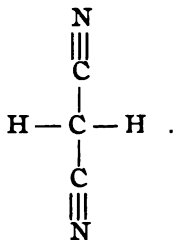
In the foregoing table, it will be observed that, with but one exception, the dielectric constants of the compounds of any homologous series decrease with increase of molecular weight. In the case of methyl mustard oil (the exception referred to), the anomaly is presumably due to the much higher temperature at which the determination was made. That the temperature coefficient of inductive capacity is negative seems to be an invariable rule; and the fact that allyl and phenyl mustard oils, which though of course not homologues of the aliphatic compounds, are of higher molecular weight, have lower dielectric constants, serves to bear out in some measure this explanation.

The fact, that the dielectric constant decreases with increasing molecular weight, was first observed by Tereschin.<sup>1</sup> Schlundt<sup>2</sup> also found it to be the case with all compounds investigated by him.

Viewed in this light, the high constant of malonic nitrile is peculiarly interesting. Schlundt<sup>3</sup> found that liquid cyanogen had the remarkable low dielectric constant of 2.52, and ethylene cyanide the very high constant of 61.2. Considered from the point of view of their structural formulæ, the dielectric constants of these substances present some curious features. The formula generally given for cyanogen is:



The formula for malonic nitrile is:

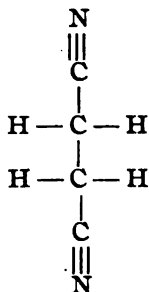


<sup>1</sup> Wied. Ann. 36, 792 (1889).

<sup>2</sup> Bull. Univ. of Wis., Science Series, 2, 376 (1901).

<sup>3</sup> Ibid. 2, 372 (1901).

For ethylene cyanide it is:



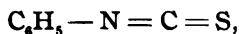
It will be noted that the first of the three, cyanogen, consists of two CN radicals, closely connected; the second has the two cyanogen radicals more apart from each other, and the last has them still less closely connected. These facts taken in connection with the respective dielectric constants of 2.52, 46.3, and 61.2, would indicate that the dielectric constant is dependent upon the comparative freedom of the cyanogen radicals from each other. This view explains the fact that with these particular compounds we have the dielectric constant increasing with molecular weight, instead of the usual manner of behavior. And this is further borne out by the fact that ethylene cyanide does not show an increase in dielectric constant over that of malonic nitrile equal to that of malonic nitrile over cyanogen. The increase in each case is the resultant of two tendencies — the greater separation of the cyanogen radicals tending to raise the dielectric constant, the increasing molecular weight to lower it. It is very probable that investigation of still higher homologues of the ethylene series of nitriles would show in time an actual decrease in dielectric constant with increased molecular weight, which would occur when the effect of increased molecular weight was sufficient to overcome the effect of separating the cyanogen radicals.

The behavior of the mono-cyanogen compounds also favors this explanation. In hydrocyanic acid, HCN, we have a cyanogen radical free from all other influence save that of the hydrogen. And, here, as would be expected, we have an extremely

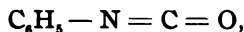
high dielectric constant, 95.<sup>1</sup> And since farther increase of molecular weight in the members of the homologous series of thiomono-cyanogen compounds can affect no farther freedom of the cyanogen radical from others of its kind, we would expect that such increase would produce a decreased dielectric constant, — as is actually the case.<sup>2</sup>

This view, that the dielectric constant of a substance is affected not only by the elements entering into its decomposition, but also by the grouping of those elements in the molecule, is confirmed by an inspection of other results given above. Ethyl sulphocyanate and ethyl mustard oils are isomers, differing only in their structural formulæ, that of the former being  $C_2H_5 - S - C \equiv N$ , of the latter,  $C_2H_5 - N = C = S$ . Since the former has a comparatively free cyanogen radical, from analogy with the other cyanides, we should expect it to have a comparatively high dielectric constant, — 31.2 it was actually determined to be. And ethyl mustard oil, which has the carbon, nitrogen and sulphur atoms quite differently arranged from those in the normal sulpho-cyanates, where the CN group is at the end of the chain, would probably have a lower dielectric constant, — 22 was the value obtained. So also methyl mustard oil has a lower dielectric constant than methyl sulphocyanate, though in this case, as above stated, the low constant of the former is presumably due, in some measure, to the temperature effect.

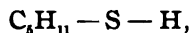
To carry the consideration farther, we have data for the comparison of phenyl mustard oil,



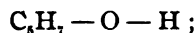
and phenylisocyanate,



amyl sulph-hydrate,



and amyl alcohol,

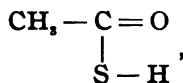


<sup>1</sup> Schlundt. Bull. Univ. of Wis., Science Series, 2, 372.

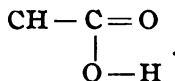
<sup>2</sup> Ibid.



thioacetic acid,



and acetic acid,



For the determination of the dielectric constants of amyl alcohol and of acetic acid, we have those of Thwing, who gives about 15 for the former, and 10.3 for the latter; these results are confirmed fairly well by other observers. On comparison, it will be found that phenyl mustard oil has 8.5 for its dielectric constant, while phenyl isocyanate has 5.56; amyl sulph-hydrate has 4.9, amyl alcohol 15 (Thwing); thioacetic acid has 17.3, acetic acid 10.3 (Thwing). Yet each of these compounds differs from that analogous to it in having sulphur in place of oxygen. That this substitution does not always produce the same general effect on the dielectric constant is evident at a glance.

The conclusion, then, appears safe, that the dielectric constant of a substance is not an additive property, but depends as much upon the grouping of the atoms as upon the character of the atoms themselves. And such a formula for the calculation of dielectric constants as that advanced by Thwing,  $R = \frac{D}{M} (a_1 K_1 + a_2 K_2 + \dots)$ , (where  $K$  is the constant of the compound,  $D$  the density,  $M$  the molecular weight,  $a_1, a_2$ , etc., the number of times each atom or group occurs in the compound,  $K_1, K_2$ , etc., constants for the respective atoms or groups), must necessarily be defective. For  $\frac{D}{M} = \frac{1}{V}$ ,  $V$  being the molecular volume of the substance; this itself was shown by Kopp to be an additive property. And any formula which makes no allowance for the arrangement of the atoms or groups in the molecule must fail of its purpose.

## PART TWO

As above stated, one of the objects of this work was to de-

termine the inductive capacity of solutions of varying content. Very little work indeed has been done in this line. Cohn and Arons<sup>1</sup> worked on the dielectric constants of very dilute aqueous sodium chloride solutions, but found that any change that took place was too slight to be perceptible by their method of experiment. In a later research Cohn<sup>2</sup> measured the refractive indices for electrical waves by a method of his own, and used the squares of these for the dielectric constants, by Maxwell's formula. He found that the dielectric constants for dilute aqueous sodium chloride solutions increased with the concentration. However, he was unable to determine the ratio of the rise. Smale,<sup>3</sup> who worked with an electrometer method devised by himself, found that with aqueous solutions of potassium chloride, hydrochloric acid, and copper sulphate, the dielectric constants increased with the concentration.

Drude<sup>4</sup> also worked with dilute aqueous sodium chloride solutions, by means of his first method, and found that the dielectric constants were not perceptibly different from those of pure water. Drude also did considerable work on solutions of liquids in liquids. So, in the case of methyl alcohol and water, he found that the dielectric constant of the solution varied directly with the percentage composition. In other words, plotting dielectric constants as ordinates, and percentage content as abscissæ, the resulting curve was a straight line. Similar results were obtained with mixtures of propionic acid and water, acetone and water, and acetone and benzene.

He also found the dielectric constants of two aqueous cane-sugar solutions, and of two gelatine solutions. In both cases the solutions had dielectric constants markedly lower than pure water.

Some work also has been done on mixtures of various organic solvents, by Linebarger,<sup>5</sup> and also by Philip,<sup>6</sup> both of

<sup>1</sup> Wied. Ann. 28, 434 (1886); and 33, 14 (1888).

<sup>2</sup> Ibid. 43, 370 (1892).

<sup>3</sup> Wied. Ann. 60, 626 (1897).

<sup>4</sup> Zeit. phys. Chem. 23, 280 (1897).

<sup>5</sup> Ibid. 20, 131 (1896).

<sup>6</sup> Ibid. 24, 18 (1897).

whom used Nernst's method. In no case did they find the dielectric constant of the solution to conform with that calculated for the mixtures from the volumetric proportions. I shall discuss this work in more detail later. Philip's results were confirmed in a later investigation by Coolidge,<sup>1</sup> who used a modification of Drude's apparatus.

Excepting some work by Thwing,<sup>2</sup> whose results do not appear to be completely borne out by other observers, the above constitutes practically all the material the writer could find on the dielectric constants of solutions. Indeed, no work appears to have been done with other than aqueous solutions, save of liquids in liquids.

In beginning this work, it was desirable to select a solvent in which several solids would be soluble, in order to obtain results directly comparable with one another. The solvent selected, carbon disulphide, possessed this feature to a marked degree, and had the additional advantage of being readily obtainable in a sufficiently pure state for my purpose.

The solutions first worked with were of phosphorus and sulphur, in carbon disulphide. These two solutes served my purpose very well, owing to their great solubility. Solutions of about 30 percent concentration were readily obtained with both.

In addition to these two solutions, solutions of menthol in benzene, carbon disulphide, and acetonitrile, and of camphor in benzene and carbon disulphide, and one solution of sulphur in sulphur monochloride, were worked with. The solutes in the first list are all elemental in character, and by the use of camphor and menthol as solutes any possible difference in behavior between compounds and elementary substances might be brought out. The reasons for the somewhat peculiar choice of solvents are as follows. By the use of benzene and carbon disulphide as solvents for the same solutes, it would be possible to ascertain whether or not the inductive capacity of the dissolved substance was independent of the solvent. However, as both benzene and carbon disulphide are substances of low dielectric constant, their

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<sup>1</sup> Wied. Ann. 69, 146 (1899).

<sup>2</sup> Phys. Rev. 2, 35 (1894).

behavior as solvents might not be thoroughly typical. Acetonitrile, which has 36.5 for its dielectric constant,<sup>1</sup> therefore was used as a fourth solvent, to render the investigation more general.

The materials used to make up the solutions were as follows : The carbon disulphide was obtained from Bausch and Lomb, and was their "pure" product. While presumably not of absolute purity, any impurities that might have been present were not of a nature to affect its dielectric constant, which was found to be 2.65 at 19°, which agrees quite well with Drude's determination of 2.64 at 17°.

Roll sulphur as obtained from Schuchardt was used. The phosphorus was also from Schuchardt, and was the purest the laboratory afforded. One source of contamination occurred here, namely, absolute dryness of the phosphorus, before its introduction into the solvent, was extremely difficult to secure, and undoubtedly a considerable amount of water was introduced into the carbon disulphide along with the phosphorus. To overcome this difficulty, fused calcium chloride was added, and the whole allowed to stand several days before determinations were made. To ascertain if at the end of this period water was still present in the solution, the latter was tested for its electrical conductivity; it was found to conduct no better than the dry solvent alone. Also, a determination was made of the dielectric constant of carbon disulphide that had been covered with water for sixty hours, after being shaken up with it; the difference between its constant and that of the dry solvent was found to be within the limit of experimental error.

The menthol and camphor were Schuchardt's pure preparation. The acetonitrile was from Schuchardt; it had been distilled from phosphorus pentoxide by Prof. Kahlenberg, and was found to boil at 80.9°, under 745 mm pressure.

The results obtained are given here in tabular form.

Only one solution of sulphur in sulphur monochloride was investigated. It was made up from Schuchardt's preparation of the solvent, the dielectric constant of which was found to be

<sup>1</sup> Schlundt. *Bull. Univ. of Wis., Science Series*, 2, 663 (1901).

I.  
Sulphur in Carbon Disulphide

Percent sulphur	D. C.	Temp.
0.0	2.65	19°
3.2	2.55	19°
5.84	2.37	19°
11.56	2.15	19°
27.26	2.08	19.5°
28.8	2.05	18°

II.  
Phosphorus in Carbon Disulphide

Percent phosphorus	D. C.	Temp.
0.0	2.65	19°
3.73	2.76	18°
12.0	3.15	18°
19.9	3.35	18°
27.0	3.4	18°

III.  
Menthol in Benzene

Percent menthol	D. C.	Temp.
0.0	2.25	24°
8.2	3.05	23°
17.8	3.7	22.5°
19.0	3.82	22.5°
29.3	5.0	23°
31.7	4.9	24°

IV.  
Menthol in Carbon Disulphide

Percent methol	D. C.	Temp.
0.0	2.65	19°
5.4	2.8	24°
11.5	3.25	24°
16.06	3.8	23.5°
22.1	4.2	24°
28.56	4.7	24°

## V.

## Menthol in Acetonitrile

Percent menthol	D. C.	Temp.
0.0	36.5	21°
7.55	32.3	23°
12.7	29.0	23.5°
20.2	24.0	23.5°
25.2	22.5	23.5°
30.23	19.5	23°

## VI.

## Camphor in Benzene

Percent camphor	D. C.	Temp.
0.0	2.25	24°
6.8	2.63	24°
11.4	3.15	24°
13.7	3.20	24°
19.5	4.4	23.5°
26.8	6.5	23°
29.4	7.25	24°

## VII.

## Camphor in Carbon Disulphide

Percent camphor	D. C.	Temp.
0.0	2.65	19°
7.24	2.85	22.5°
10.74	3.0	22°
15.5	3.65	21°
20.1	5.0	24°
25.3	5.82	21.5°

4.85 at 23° (Schludt, 4.8 at 22°). The solution was approximately 13 percent concentration, and was found to have 3.6 for its d. c., at 23°.

### Discussion of Results

In the work by Linebarger<sup>1</sup> previously referred to, he showed that for a considerable number of solutions of various organic liquids, the dielectric constant in no case agreed with that calculated from the volume percentage, by the formula

$$K = \frac{K_1 V_1 + K_2 V_2}{V_1 + V_2}.$$

This formula had previously been advanced by Silberstein,<sup>2</sup> who found it borne out by solutions of benzene and phenyl acetate measured by him.

In a later article Philip,<sup>3</sup> working along similar lines to those of Linebarger, confirmed the latter's results with other solutions. Linebarger had found that with all solutions save those containing ethyl ether, the dielectric constant as calculated was higher than the observed constant; the reverse was true for solutions having ethyl ether as one component. Among the solutions investigated by Philip was a series made up of mixtures of ethyl ether and chloroform. With these he found that the dielectric constants of some of the solutions were actually higher than those of either component.

Drude,<sup>4</sup> in discussing his results on solutions, endeavored to explain the poor agreement between calculated and observed values on the basis of allowing for the contraction accompanying the mixture of the two components. Even granting that such contraction in the case of the ether solutions (or expansion in the case of other solutions), always takes place, correction for it in the formula as given above does not suffice to bring the dielectric constant to its observed value. Drude states, "Diese Differenz kann man nur heben, wenn man annimmt, dass bei einer oder beiden Komponenten des Gemisches die Dielektrizitätskonstante grösser ist, als in ungemischtem Zustande. Diese Annahme ist ja schon an sich bei beträchtlichen Kontraktionen plausibel."

<sup>1</sup> Zeit. phys. Chem. 20, 131 (1896).

<sup>2</sup> Wied. Ann. 56, 661 (1895).

<sup>3</sup> Zeit. phys. Chem. 24, 18 (1897).

<sup>4</sup> Ibid. 23, 301 (1897).

This explanation might be sufficient for the case of liquids in liquids. But Drude himself found that on calculating the dielectric constant of cane-sugar from the results obtained by him with two sugar solutions, he got in the case of the more dilute solution 35.2, with the stronger solution 14.3, for the constant of the pure sugar. This difference is no longer explicable, either directly or indirectly, on the basis of contraction of the solution, since none takes place, as he himself states. However, both solutions exhibited anomalous absorption to a considerable degree, and Drude believed this to be the cause of the lack of agreement.

The solutions employed by the writer were not of such a character as to exhibit anomalous absorption: Hence any difference that might occur between calculated and observed results would certainly not be explicable on that basis. To show that such difference actually occurred, I chose several solutions at random from those investigated, and calculated the dielectric constant for the solute from those of the solvent and of the solution, by the above formula. The values of the  $V$ 's, it is true, were not precisely correct, as they were found by dividing the respective percentages by the densities, the latter being taken from Landolt and Börnstein's table, for the temperature nearest those at which the determinations were made. The calculated results so obtained were so at variance as to make their insertion here useless. In several instances, indeed, they were actually negative, notably for some of the sulphur solutions, and for some of the solutions of menthol in the various solvents.

Of course, from the very character of the dielectric constant, a negative result is an absurdity. And any attempt to explain such an anomaly, even on the basis of change of volume of the resulting solution, would necessarily pre-suppose changes altogether greater than actually occur. Philip also endeavored to calculate the dielectric constant of a solution from formulæ based on Maxwell's law that the dielectric constant equals the square of the refractive index, starting from optical formulæ. As he found that calculated results did not agree very closely



with those observed, particularly with solvents of rather high inductive capacity, it would be useless to take up the matter here.

In view of the fact that Drude obtained practically straight line curves for his solutions of liquids in liquids, plotting dielectric constant and percentage content, it might be of interest to present some of the curves so obtained with the solutions investigated here. In Fig. 5 are shown the curves obtained with carbon disulphide

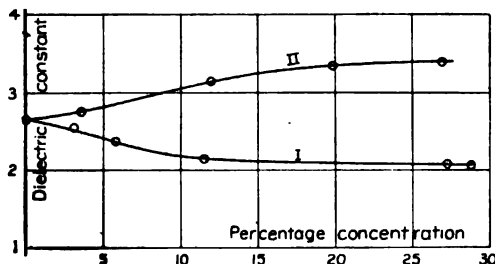


Fig. 5

- I. Sulphur in carbon disulphide  
II. Phosphorus in carbon disulphide

solutions of sulphur and phosphorus. It will be noted that both curves apparently approach parallelism with the axis of abscissæ as the concentration increases; this would seem to indicate that the first addition of these solutes produce greater differences in inductive capacity than do subsequent ones. That the approximate parallelism of the curve to the axis mentioned indicates that the solution has reached almost the inductive capacity of the solute itself, is not a perfectly safe conclusion. However, the dielectric constant of solid sulphur is placed by the majority of observers between 2 and 4, and, if it be assumed that the density of dissolved sulphur be less than that in the solid state, the result obtained from the solutions agrees fairly well with the other. As regards phosphorus, data as to its specific inductive capacity are lacking. If it is safe to reason from analogy to the sulphur curve, the dielectric constant of phosphorus would be at most somewhat less than 5.

Fig. 6 shows the curves obtained from the carbon disulphide and benzene solutions of menthol. It will be noted that the

benzene curve is almost a straight line; the carbon disulphide curve is at first convex to the axis of abscissæ, and curves until it closely approaches the benzene curve, when it becomes practically coincident with it.

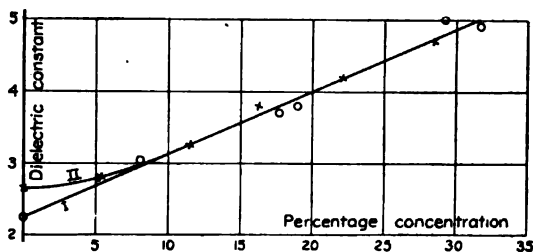


Fig. 6

I. Menthol in benzene  
II. Menthol in carbon disulphide

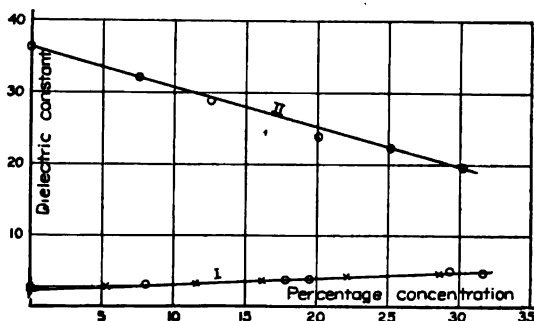


Fig. 7

I. Menthol in benzene and carbon disulphide  
II. Menthol in acetonitrile

Fig. 7 shows these curves, plotted on a smaller scale, together with the curve obtained with acetonitrile as a solvent. The fact is significant that, within the limits in which the work was done, the curves show no tendency toward convergence on the 100 percent ordinate. In the case of the benzene and carbon disulphide solutions, their practical coincidence would augur their coincidence at that point also. But the slope of the acetonitrile curve (which is, within the limits of experimental error, a straight line), is altogether too abrupt to reach the 100 percent ordinate at all. This shows that the curve must defect at some

greater concentration, just as do the sulphur and phosphorus curves, and approach parallelism to the axis of abscissæ.

However, the conclusion is safe that the curves of concentration and dielectric constant of these solutions afford no definite clue to the dielectric constant of the solute, within moderate concentration. In other words, the dielectric constant of moderately concentrated solutions is not a simple function of either the solute or of the solvent. The curves obtained with camphor dissolved in benzene and carbon disulphide are shown in Fig. 8. They show a somewhat similar behavior with regard

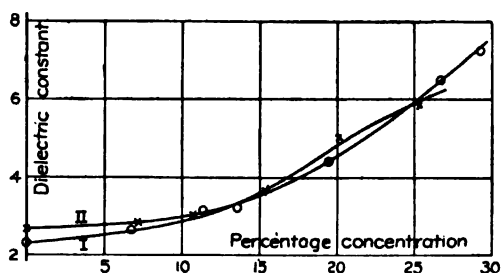


Fig. 8

I. Camphor in benzene

II. Camphor in carbon disulphide

to each other as the corresponding curves for menthol, though the coincidence of the two is less marked here. This tends to confirm the conclusion just stated.

If these results be viewed in connection with those obtained by Linebarger and by Philip, the conclusion is obvious that, as Philip puts it, they can best be explained on the basis of "intermolecular reactions" between solvent and solute. This confirms general conclusions regarding the nature of solutions, which have already been reached from work on rates of reaction, done by Prof. Kahlenberg,<sup>1</sup> and on electrical conductivities, by Dr. Patten, in this laboratory.<sup>2</sup>

The following is a brief summary of the results obtained in this research :

<sup>1</sup> Jour. Am. Chem. Soc. 25, 390 (1903).

<sup>2</sup> Jour. Phys. Chem., 5, 599 (1902).

The dielectric constants of various hitherto uninvestigated solvents, mostly sulphur compounds, have been measured.

It has been shown, notably in the case of the nitriles, that the dielectric constant is not an additive property, but is dependent to a very great degree on the relative chemical structure of the molecule.

In the case of the nitriles, it has been found that a single cyanogen radical at the end of a chain has the effect of raising the dielectric constant to an enormous degree. Two cyanogen radicals, however, in the same molecule, tend to neutralize each other, and it is only upon their separation in the molecule that the resultant raising of the inductive capacity occurs. This explains what was hitherto inexplicable, namely, the fact that while cyanogen itself has a very low specific inductive capacity, its hydrogen compound, HCN, has one of the highest dielectric constants hitherto found, and that the simple nitriles and normal sulphocyanates have high dielectric constants.

Work done on solutions of solids in liquids tends to show that :

(a) The volumetric formula advanced by Silberstein for the calculation of the dielectric constants of solutions from those of their components, while roughly approximate for solutions of liquids in liquids, is entirely inadequate when applied to solutions of solids in liquids.

(b) Only in one case, that of sulphur dissolved in carbon disulphide, did the results seem to give a clue to the dielectric constant of the solute.

(c) In cases where several solvents were used with the same solute, the dielectric constants of the mixture did not indicate that the solute exerted a similar influence in each case. And this phenomenon points directly to the conclusion that the dielectric constant of a solution is not a simple function of either constituent, but is due to an indefinite compound, i. e., a compound according to variable proportions, resulting from combination of the constituents.

In conclusion, I wish to express my deep sense of obligation to Prof. Kahlenberg, without whose unfailing interest and timely advice, the work would have been well nigh impossible. His encouragement and suggestions lightened the task of much of its difficulty, and I am glad of this opportunity to acknowledge my indebtedness to him.

*Laboratory of Physical Chemistry,  
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Madison, June, 1903.*

[CONTRIBUTIONS FROM THE CRYOGENIC LABORATORY OF WESLEYAN UNIVERSITY, No. 1.]

## THE RESISTANCE OF GLASS TUBING TO BURSTING PRESSURE

BY W. P. BRADLEY AND A. W. BROWNE

Scientific literature contains but little direct information concerning the power of glass to withstand bursting pressure. The tensile strength of different kinds of glass has been determined, it is true, by v. Kowalski<sup>1</sup> and by Winkelmann and Schott,<sup>2</sup> after the usual method of determining the tenacity of metals. But while it is possible from data such as these to calculate the theoretical bursting pressure for tubes of given dimensions, it is not safe to rely upon results so obtained. A natural conclusion from such data would be that a thick-walled tube should invariably stand a higher pressure than one with walls not so thick. Our first experience with glass tubing under pressure indicated that this was by no means strictly true. Pieces of barometer tubing, obtained but a short time before from the dealers, though of unknown make, burst invariably at a pressure below 160 atmospheres, at the first trial. Moreover, a sample once tested to about 100 atmospheres would never withstand as much again, but would sometimes burst, during subsequent tests, at ridiculously low pressures. In some cases, the tubing would break spontaneously into many pieces, within a few hours after the first test had been made. On one occasion, a tube which had cracked in two over night, was repeatedly heard during the working hours of the day following to snap suddenly as it continued its process of self-demolition.

This experience of ours, combined with that of Mendelejeff,<sup>3</sup> convinced us that it was a fundamental mistake to select tubes of great thickness of wall for high pressure work.

<sup>1</sup> Wied. Ann. 36, 307 (1889).

<sup>2</sup> Ibid. 51, 697 (1894).

<sup>3</sup> Ber. chem. Ges. Berlin, 7, 126 (1874).

A little later, having in hand some inquiries relative to the so-called "critical" phenomena of gases,<sup>1</sup> we instituted the tests of which the results are given below. They have proved of great value to us, and we publish them in the hope that they may be of wider service. They make no claim to completeness, but they do show in some measure, as we believe, what may reasonably be expected of a few of the more common varieties of glass, when proper care is exercised in the sampling, sealing and mounting.

Seven sorts of glass were tested in all, as follows :—

- I. Bohemian — 6 samples.
- II. Jena — 11 samples.
- III. Jena compound — 2 samples only.
- IV. Soft glass of Greiner & Friedrichs — 7 samples.
- V. Soft glass of E. Gundelach — 11 samples.
- VI. "American." A lead glass, which blackened easily in sealing — 6 samples.
- VII. A comparatively new glass of Whittall Tatum Co., called by them "flint", not because of its composition, as the manufacturers inform us, but because it is made at the factory from which they derive their ordinary flint glass. It is a calcium glass and was included in the tests for the reason that beakers, flasks, and test-tubes made of it had given eminent satisfaction in the work of our analytical classes. It is clear and brilliant and of uniform texture. It can be worked, if need be, in the Bunsen flame, and yet does not soften as suddenly nor at as low a temperature as soft German glass, — 23 samples, of which twelve were of nearly uniform thickness of wall with varying bore, and eleven, of nearly uniform bore with varying wall.

All of the samples of Nos. I–VI were furnished us at our request by Eimer & Amend, and were carefully selected for these tests from their stock. The specimens of No. VII were sent, also at our request, by the manufacturers.<sup>2</sup>

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<sup>1</sup> The inquiries mentioned, to which the material contained in this paper was preliminary, have received the support of a grant from the Elizabeth Thompson Science Fund.

<sup>2</sup> Our thanks are due to both of these firms for their kindness, as well as for the care with which they have met our requirements.

*The Sampling.* — Pains were taken in sampling, with good degree of success, to secure the following characteristics: — (a) strictly circular cross-section; (b) perfect centering of the bore; and (c) freedom from taper. The greatest observed deviation from (a), — difference between the longest and the shortest diameter of any single cross-section, — was 1/10 mm. There was no appreciable eccentricity of bore, and the maximum taper discovered corresponded to 1.5 mm per meter of length. From first to last the same care was observed as if each tube were intended for use in an elaborate experiment. All tubes were rejected which contained any knots, streaks, or other visible inequalities of texture.

*The Measurement.* — A wedge of sheet metal, 10 cm long and 1 cm wide at the base, was carefully graduated. Each centimeter in the length of this wedge corresponds to a millimeter of width. To determine the internal diameter of a tube, the wedge was inserted as far as possible, with care not to chip the sharp edges of the glass, and the length of the inserted portion was read. One tenth of this reading was the diameter sought. A negative strip served to measure external diameters in a similar way.

All the tubes were of the same length, 20 cm.

Whenever the slightest inequalities were noted in any tube, the thinnest part of the wall and the greatest internal diameter were made the basis of computation. If the tube tapered, it was mounted in such a way that the widest, and therefore the weakest end was exposed to the bursting pressure. The practical object of the tests was of course to determine the minimum rather than the maximum strength of the tube.

*The Sealing.* — In preparation for the test, one end of the sample was sealed in such a way as to secure a very regular, hemispherical tip, of the same thickness as the rest of the tube, and quite free from any knot of glass at the center. The other end was slightly enlarged for a length of 2–3 mm. Both were annealed with very great care.

*The Mounting.* — Each tube was mounted in turn in the cap of a Cailletet apparatus in the manner displayed in Fig. 1.



A is the cap, which is traversed by a bore of varying diameter. That at the top is 1.5 cm ; that at the bottom is twice as great.

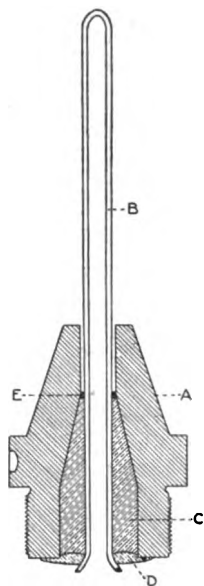


Fig. 1

The central section is conical. B is the tube to be tested. At C (and D) is the wax by means of which the joint is made between the tube and the cap.

Many fruitless weeks were spent in attempts to secure a wax of such consistency as to render a joint at once tight and strong. It was not difficult to obtain a mixture of sufficient rigidity, or one which would adhere to the surface of glass or of metal. But these qualities appeared in practice to be mutually exclusive. A wax which would stick and never let go was always too soft for the pressure. If rigid enough not to flow under pressure, it would almost invariably leak either next to the wax or the metal. At last in despair we divided the problem and used two sorts of wax, — one to resist pressure, and one to stick. Since then, trouble from this source has practically ceased.

The first wax is composed of 5 parts resin,  $\frac{1}{2}$  a part of beeswax, and 1 part Venetian red, thoroughly melted and mixed.<sup>1</sup> This composition melts easily, flows thinly when melted, and sets slowly, — three most desirable qualities. Its usefulness, however, is limited to temperatures below 20° C. In summer weather it is unserviceable, as it yields gradually to pressure. For long resistance to pressure in warm weather, the following is suggested — 2 parts each of resin and shellac, and 1 part of Venetian red. This never yields at any ordinary temperature, but is much less convenient to use, being thicker when melted. It is more difficult to pour, and care is required in melting, as it is easily scorched.

<sup>1</sup> It will be noted that this wax resembles that suggested for a similar purpose by Faraday many years ago (Faraday, *Chemical Manipulation*, 1st Amer. Ed., page 507). It differs in containing one-half as much beeswax.

As has been said, no such composition as these can be relied upon to furnish a *tight* joint. The other wax, whose function is adhesion, is made by melting together Venice turpentine and a very little beeswax. Exact proportions are difficult to state, as the consistency of the turpentine is somewhat variable, and much depends on the temperature at which the mixture is to be used. The correct proportions are secured, however, when there is enough beeswax to prevent it from flowing at room temperature, and not enough to cause it to chip under a knife blade. When properly made, moreover, it is not sticky when cold. Of course, like the hard wax, it is melted before use. It is represented at D in Fig. 1. E is a rubber band or washer, which serves to hold the pressure tube in position during the mounting, as well as to retain the melted wax until it has set.

The general order of procedure to be followed in mounting a tube will be sufficiently clear no doubt from what has been said. One precaution, however, is deserving of careful observance. The setting of the hard wax is attended by considerable contraction. This may result, through inattention, in a cavity more or less deep, which will usually be found rather close to the glass, and may give rise to lateral strain when pressure is applied. It is of great importance that the hard wax be symmetrically disposed as well as uniform in texture, if the tube is to develop its maximum power of resistance during the test. For this reason, to forestall the formation of cavities, it is well to introduce the molten hard wax in two, or even in three portions, allowing each to stiffen before the next is poured. The surface of the uppermost layer may finally be melted smooth by the use of a hot nail. The soft wax should not be poured till the other is quite hard, nor then, unless the surfaces of the metal and glass have been rubbed perfectly clean.

In this way, but little care is required to make a joint which will hold through almost any test to which it may be subjected. In connection with the inquiries already alluded to, such a joint has successfully withstood, for two or three weeks at a time, a pressure of 70-80 atm, — a test far more exacting

than sudden exposure for a few moments to a pressure many times as great.

It may be remarked at this point, in parenthesis, that experience has led us to deem it an error to mount tubes of glass in snugly fitting collars, which leave but a narrow space in which to form the joint. Mounted in such a way, a tube can seldom exhibit its normal resistance. When a newly mounted tube is first exposed to the test, a sort of click is often heard, which sounds as if the glass itself had snapped within the wax. If hard wax only were used, this click would surely be followed at once by a leak. What has happened, however, is not, as yet, a break in the glass, much less a cracking of the wax itself, but a rupture of the original contact between the hard wax and the metal. Such a rupture, however, is the occasion of a sudden readjustment of the wax to the metal, and this may easily lead at once to such a lateral strain as shall result in prematurely breaking the tube under subsequent increase of pressure.<sup>1</sup> On the contrary, if the layer of wax be sufficiently thick, its readjustment produces no such effect. Lateral strains, if any, are borne in this case by the wax rather than by the glass.

*The Testing.*—The tube, when properly mounted, was filled with water. The cap with its contents was screwed into place in the Cailletet apparatus, which also was filled with water. Pressure was then applied in the usual way by means of a powerful pump. To allow more convenient reading of the gauge, it was found advisable to raise the pressure by successive increments of about 5 atm, waiting somewhat between each accession. It may be that this procedure was advantageous also in allowing opportunity for the wax to adjust itself to the new conditions.

*The Nature of the Rupture.*—As the pressure was strictly hydrostatic, the rupture of the tube was not attended by a loud

<sup>1</sup> In certain of our preliminary tests, in which the cap was filled throughout its entire length with wax, including the narrow section at the top, such mishances were rather frequent. A tube would often burst at a pressure abnormally low, and subsequent examination would show that it was broken square across in the upper third of the wax.

report. At the most, a sort of a semi-metallic click or snap was heard, scarcely louder than that produced by breaking a tube in the hands at a file mark. Indeed, the comparative gentleness of the rupture made it possible in a simple way to keep the fragments of glass for the most part in place. It was sufficient to wrap the tube with a few thicknesses of cheese cloth before the pressure was applied, and after the rupture to unroll the same with a little caution. Of course the pieces were always found fallen together in this case, but longitudinally they still retained their proper relations. Even the finest fragments were retained by the cloth, which was never found punctured.

In the case of a few tubes still better results were obtained. These had been encircled at intervals of about 1.5 cm with very narrow strips of gummed paper before the cloth wrapping was applied. Surprising as it may seem, these frail bands held nearly the entire tube together except in the immediate neighborhood of the center of rupture. At that point the tube divided into two parts, but each of these was found to be cylindrical still, when unwrapped, though splintered from end to end. In most cases, the two parts could still be fitted together with a little patience.

Figure 2 illustrates very closely the appearance of such a tube when reconstructed. At the point A most of the glass is lacking for the reason that it was reduced to powder. This was the center of the rupture. About this center lies an area which is roughly annular in shape and which contains small trapezoidal fragments, or somewhat larger pieces from which such fragments have been broken. Still further outward the fragments are of much larger dimensions. It is interesting to note that at their tips, whether blunted or sharp, invariably point toward the center at A. It would appear in fact that glass tubes which burst under hydrostatic pressure become cracked in a manner quite similar to that displayed by a pane of window glass when perforated by a bullet. Here also there is a hole at the center of disturbance, small fragments beyond, and outside of



Fig. 2

all, cracks radiating from the center. In the case of the tubes, however, some of these cracks are necessarily spiral.

Very rarely indeed was any other type of rupture noticed than the one just described. Once, to be sure, the entire upper part of a tube broke cleanly away from the rest, leaving the circular ends which result when a piece of good glass is filed and skillfully broken. The flying piece, carrying the cloth with it, rose a foot or so in the air and fell in perfect condition upon the desk. The bursting pressure agreed so well with that which the data from other tubes of the same glass would have led one to expect, that it seems quite unlikely that this peculiar break is to be accounted for by any imperfection in the glass or accidental scratch sustained before the test.

The location of the center of the rupture was rather interesting. In most cases it was not especially near to either end of the tube, but rather in the central third of its length. The fact is significant. It is clear that the tubes did not burst, as a rule, because of imperfect sealing or of insufficient annealing, or because of any strain which was due to the manner of mounting. On the contrary, the conclusion seems irresistible that the narrower top of the tube and the wax at the bottom served in some degree to strengthen and protect the glass in their immediate vicinity. Indeed, the question arises whether their influence may not have been felt, to some extent at least, even in the center of the tube, so that the bursting pressure was raised somewhat thereby. It seems hardly possible that such an influence could have amounted to very much at a distance of 5-7 cm. But if these tests were to be repeated, it might be advisable to cut the tubes of somewhat greater length.

To draw any conclusion from the facts observed in the case of hydrostatic pressure as to the nature of bursting under pneumatic pressure would of course be extremely hazardous. It is natural to infer, however, that the pulverized area, *A*, and the ring of fragments around it, if one existed at all, would each be much more extensive. Whether there would be any pieces of size outside of these, and whether they would be more or less

wedge-shaped, supposing that they could be shielded from secondary rupture by collision, it is quite impossible to say. On the other hand, the pulverized condition of a Carius tube after explosion is no necessary indication of the direct effect of that explosion. Rather does it show the certain result of collision at extremely high velocity between glass and a solid obstacle.

One other point should be mentioned before the numerical results of the tests are presented. As already mentioned, the pressure was applied in small increments, with a short period of rest between each addition. It is noteworthy that many tubes did not burst while the pressure was rising, but during the period of constant pressure which followed. This, also, may be a fact of some significance, as it suggests a deterioration of the glass when near its limit of resistance.

Below are given, for each sort of glass used, a table containing the data of the tests, and a diagram in which the results are plotted. In each,  $W$  denotes thickness of wall;  $B$ , the internal diameter; and  $P$ , the bursting pressure in atmospheres. Columns 1-4 in the tables explain themselves. As the bursting pressure is found in general to vary directly as the thickness of the wall and inversely as the bore, the values of  $W/B$  are entered in Column 5. Still further to facilitate comparison not only between individual tubes in each table, but also between different sorts of glass, a sixth column is added which contains the values of  $PB/W$ , that is, the bursting pressure in atmospheres when  $W/B = 1$ .

TABLE A.—Bohemian glass

Number of tube	Wall $W$ mm.	Bore $B$ mm.	Bursting pressure. Atm.	$W/B$	$PB/W$ Atm.
1	0.925	9.70	49.0	0.0954	514
2	1.550	8.20	134.5	0.1890	712
3	1.025	8.65	67.5	0.1185	570
4	0.950	6.50	98.0	0.1462	670
5	0.975	5.80	85.5	0.1681	509
6	0.950	4.20	177.5	0.2262	785
Average $PB/W$					627

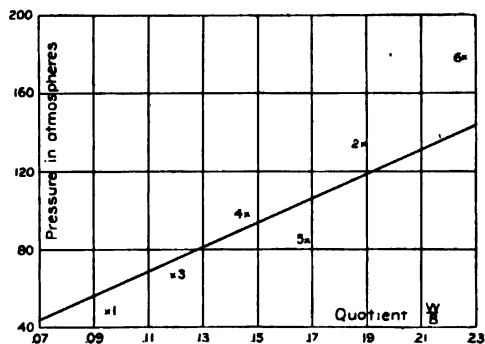


Diagram A

Bohemian

TABLE B.—Jena glass (including Jena compound)

Number of tube	Wall W mm.	Bore B mm.	Bursting pressure. Atm.	W/B	PB/W Atm.
1	0.900	11.20	122.5	0.0804	1524
2	0.625	11.45	55.0	0.0546	1007
3	0.450	9.50	61.5	0.0474	1297
4	0.475	9.45	98.0	0.0503	1948
5	0.700	6.50	116.3	0.1077	1079
6	0.675	6.11	122.5	0.1107	1107
7	0.750	5.90	116.4	0.1271	915
8	0.450	6.40	92.0	0.0703	1305
9	0.550	6.10	116.3	0.0902	1289
10	1.200	4.20	233.0	0.2857	816
11	0.700	3.90	189.5	0.1795	1056
Average PB/W					1213 <sup>†</sup>
A <sup>1</sup>	0.900	9.90	134.5	0.0909	1480
B	1.150	8.65	162.0	0.1330	1218
Average PB/W					1350

<sup>†</sup> Nos. A and B were the only specimens of Jena compound at our disposal. As a separate table and diagram would have meant but little, they were accordingly classed with ordinary Jena, but with special designation. It should be said, however, that in the diagram these two specimens were left out of account in the tracing of the curve.

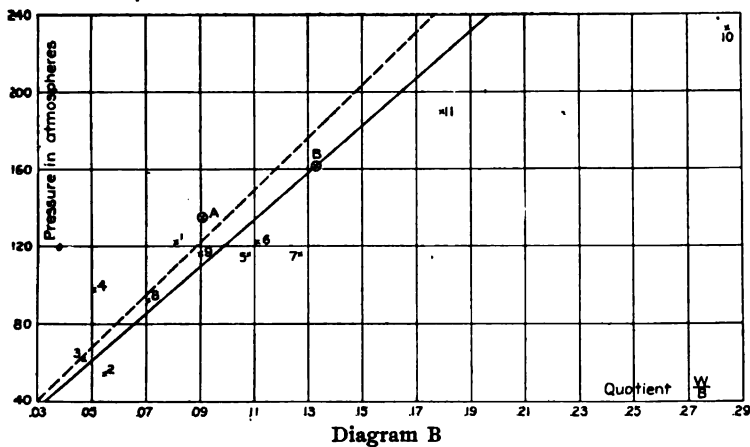


TABLE C.—Greiner and Friedrichs

Number of tube	Wall W mm.	Bore B mm.	Bursting pressure. Atm.	W/B	PB/W Atm.
1	0.775	11.45	98.0	0.0678	1445
2	0.650	9.20	110.0	0.0707	1556
3	0.900	6.70	153.0	0.1343	1139
4	0.575	6.60	104.0	0.0871	1194
5	0.825	5.80	165.0	0.1422	1160
6	0.800	4.30	92.0	0.1860	495
7	1.150	2.85	165.0	0.4035	409

Average PB/W

1057

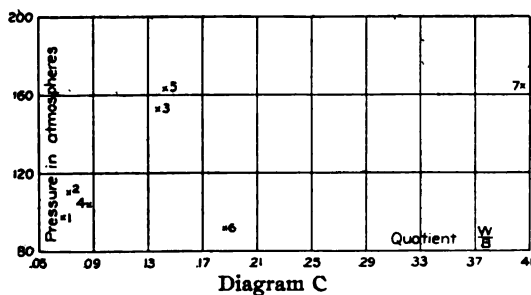




TABLE D.—E. Gundelach

Number of tube	Wall W mm.	Bore B mm.	Bursting pressure. Atm.	W/B	PB/W Atm.
1	0.650	10.70	116.0	0.0607	1910
2	0.875	10.40	135.0	0.0841	1605
3	1.350	7.70	67.5	0.1753	385
4	0.500	9.50	110.0	0.0526	2090
5	1.050	6.40	208.0	0.1641	1268
6	0.575	6.60	128.0	0.0871	1469
7	0.750	3.80	214.0	0.1974	1084
8	1.400	4.40	177.0	0.3182	556
9	0.500	4.60	257.0	0.1087	2364
10	0.850	3.30	49.0	0.2576	190
11	2.400	4.70	227.0	0.5106	445
Average PB/W					1215

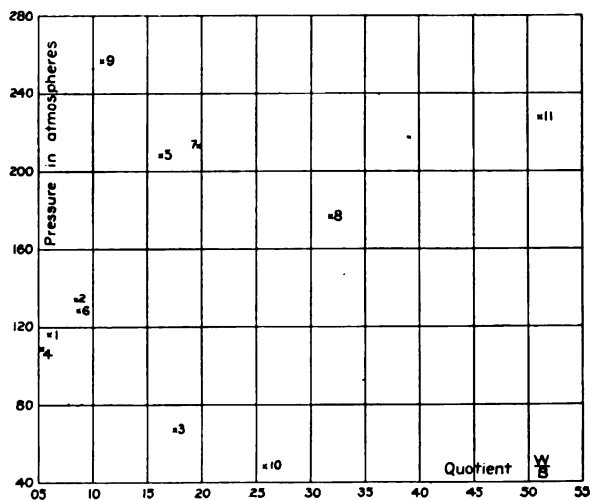
Diagram D  
E. Gundelach

TABLE E.—“ American ” glass

Number of tube	Wall W mm.	Bore B mm.	Bursting pressure. Atm.	W/B	PB/W Atm.
1	1.000	8.10	159.0	0.1235	1287
2	1.125	7.70	190.0	0.1461	1300
3	0.675	7.60	116.5	0.0888	1342
4	0.825	6.40	183.5	0.1289	1424
5	1.050	5.80	196.0	0.1810	1083
6	1.200	5.80	245.0	0.2069	1184
Average PB/W					1270

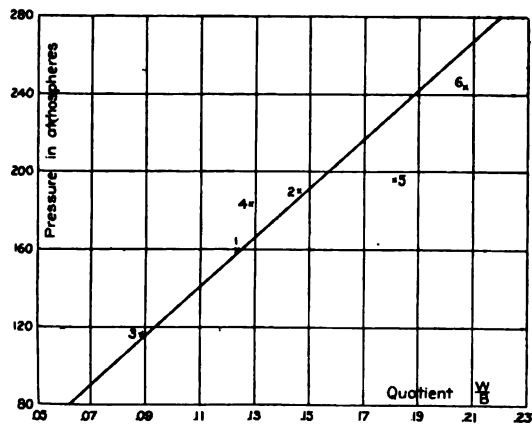


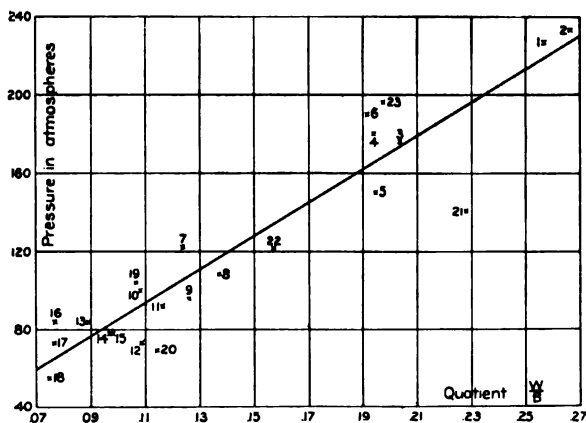
Diagram E  
American

TABLE F.—Whitall Tatum Co.

Number of tube	Wall W mm.	Bore B mm.	Bursting pressure. Atm.	W/B	PB/W Atm.
1	1.12	4.36	227.0	0.2569	884
2	1.15	4.31	233.5	0.2668	875
3	0.95	4.65	177.0	0.2043	866
4	1.07	5.53	180.5	0.1935	933
5	1.09	5.63	147.0	0.1936	759
6	1.09	5.70	189.5	0.1912	991
7	0.98	7.94	122.5	0.1237	990
8	1.08	8.02	103.5	0.1347	768
9	1.01	7.99	96.5	0.1264	763
10	1.03	9.52	99.0	0.1082	915
11	1.12	9.63	92.0	0.1163	791
12	1.05	9.63	73.5	0.1090	674
13	0.72	8.10	84.0	0.0889	945
14	0.78	8.06	79.5	0.0968	822
15	0.79	8.14	79.5	0.0971	819
16	0.62	8.10	84.0	0.0765	1097
17	0.62	8.10	73.5	0.0765	960
18	0.60	8.06	55.0	0.0744	739
19	0.89	8.36	103.5	0.1065	972
20	0.93	8.14	70.5	0.1143	617
21	1.87	8.20	141.0	0.2281	618
22	1.40	9.06	122.5	0.1545	793
23	1.59	8.07	196.0	0.1970	995

Average PB/W

851

Diagram F  
W. T. Co. "Flint"

In each table an average of the values of Column 6 will be found at the foot of the column. For convenience, this average may be called the "norm" of the glass to which the table belongs. It represents the relative strength of the glass, so far as the tests have shown it.

A study of these 'norms' is instructive. They are grouped in Column 2 of Table G.

TABLE G.—Comparison of Glasses

Glass	Section I. Strength	Section II. Reliability	
	Av. PB/W Atm.	Variation. Average. Percent	Variation. Max. Percent
Bohemian	627	15.3	+25.2
Jena	1213	19.5	+60.6
Gr. & F.	1057	32.7	-61.3
Gundelach	1215	51.1	+94.6
American	1270	7.2	-14.7
W. T. Co.	851	11.3	+28.9

TABLE G—Comparison of Glasses (*Continued*)

Glass	Section III. Erratic tubes			
	Positive variation		Negative variation	
	Percent	Number	Percent	Number
Bohemian	41	1	59	2
Jena	60	2	40	2
Gr. & F.	42	2	58	2
Gundelach	45	3	55	4
American	70	2	30	1
W. T. Co.	62	6	38	4

As will be seen, the glasses fall naturally into two divisions, — those whose norms are well above 1000 atm, comprising the soft glasses and the Jena; and those which are considerably under that value, — the Bohemian and the calcium glass of Whitall Tatum Co. The hardest glass has much the lowest

norm, while the lead glass has the highest, though it differs so little from the Jena and the soft glass of E. Gundelach, that further tests might easily reverse the order of the three.

It is clear, however, that the norms are far from telling the whole story. The reliability of a glass depends not only upon the average strength shown by the samples, but fully as much, if not more, upon the extent to which individual tubes vary from the average. Section II of the table contains data upon this point. Column 1 gives, in percent, the average variation of all the tubes of each kind from their norm, while Column 2 contains similarly the maximum variation exhibited by any one sample. The sign prefixed to the values of Column 2 indicates the direction of the variation, — the positive sign representing strength, and the negative sign, weakness.

The extent to which individual tubes vary from their norm appears to differ widely for the different sorts of glass. The lead glass is much more clearly the leader in point of reliability than it is in strength. In fact, if the table were based upon a larger number of samples, the reliability of this glass might well be considered astonishing. The most erratic tube was only 15 percent below the theoretical strength. The glass of Whitall Tatum Co. is a close second, and the Bohemian and Jena follow at about equal intervals. At a considerable distance behind these come the soft glasses of Greiner and Friedrichs and of E. Gundelach, differing widely from each other.<sup>1</sup> A tube of the last named actually refused to burst until the pressure was nearly twice as great as that calculated for it. This type of glass possesses great strength but is very erratic.

The case of the tube just mentioned, which showed such

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<sup>1</sup> In the diagrams which have already been given, a "normal" line has been drawn wherever the reliability of the glass seems to warrant. This line, as its name indicates, cuts the origin of the axis if extended in one direction, and in the other passes through a point corresponding to  $W/B = 1$ , and to the value of  $PB/W$  for the glass considered. In diagram B the continuous line is the "normal" for the Jena glass, and the dotted line for the Jena compound. From the normal line may be read what strength may be expected of a tube for which the value of  $W/B$  is known, or conversely, the ratio of  $W$  to  $B$  which will enable a tube to withstand any given pressure.

phenomenal and unexpected strength, originally suggested Section III of the table. This might perhaps not unfittingly be designated the section of "luck". It has reference only to those erratic tubes whose strength differs by more than the average (Section II, Column 1) from their norm, — in short, those which constitute the greatest source of uncertainty in their class. For each of these tubes the difference was taken, with due regard to sign, between the value  $PB/W$  and the norm. The respective sums of the positive and of the negative differences were then reckoned in percentages of their combined total, and entered in Columns 1 and 3. The corresponding number of tubes involved may be found in Columns 2 and 4.

To make quite clear the import of this section, the case of the Jena glass will serve. The tubes of this glass whose strength differed from the norm by more than the average variation of all the tubes (19.5 percent, Section II, Column 1), were four in number. Two of these were stronger, and two were weaker, than the average. But the strength of the former pair taken together was more abnormal than the weakness of the latter in the ratio 60 : 40. In this case luck lies upon the right side, so far as the tests show it. The same may be said in general, though in varying degree, of the "American", and of the glass of Whittall Tatum Co. "Freak" tubes of these makes apparently incline to the side of strength, with the lead glass again to the fore.

Of course this section of the table is of little value as compared with the first and second. Its data are confessedly those which would be most profoundly modified by further tests. In spite of that fact it is not by any means destitute of practical interest.

In simple justice to the makers, it should be said that none of the glasses discussed in this paper was manufactured with any view to its use in work involving high pressures. Indeed, we have been unable to discover that any attention has been given, either theoretically or practically, to the conditions which make for strength in glass. In consideration of the widening

interest now manifested in work at high pressures, a thorough study of glass from this view-point would seem well worth the undertaking.

TABLE H.—Earlier Observations

No.	Author	W mm.	B mm.	P Atm.	PB/W Atm.	Kind of glass
1	Bunsen <sup>1</sup>	1.90	7.4	80	312	Green bottle glass
2	Faraday <sup>2</sup>	0.44	5.2	67	792	" "
3	"	0.89	13.5	25	379	" "
4	Coathupe <sup>3</sup>	2.31	69.9	52	1573	Ordinary white glass
5	Cailletet <sup>4</sup>	0.55	15.9	38	1099	" "
6	"	1.05	9.05	104	896	" "
7	Brunnell <sup>5</sup>	(10.00)	(18.0)	126	227	Flint glass
8	Faraday <sup>2</sup>	0.76	4.2	118	652	Green bottle glass
9	Coathupe <sup>3</sup>	4.76	28.6	105	631	
10	Andrews <sup>6</sup>	4.00	0.5	200	25	
11	Ladenburg <sup>7</sup>	3.00	2.0	(95)	(63)	
12	Amagat <sup>8</sup>	5.00	1.0	400	80	
13	Hannay & Hogarth <sup>9</sup>	3.12	0.75	880	212	
14	Olzowski <sup>10</sup>	3.00	14.0	70	327	
15	Villard <sup>11</sup>	0.75	8.0	100	1067	
16	Moissan <sup>12</sup>	2.00	6.0	a(20)	(60)	
17	"	2.00	3.0	b(100)	(150)	
18	"	2.25	1.5	300	133	
19	Stock & Hoffmann <sup>13</sup>	1.20	10.0	60	500	

In conclusion we present a number of the scattered references to the bursting pressure of glass which have come under our notice. This list includes only such as afford sufficient numerical data for the calculation of the value  $PB/W$ . Of the nineteen tubes thus tabulated, only the first six were actually burst. The rest are described by the authors in some such terms as "sufficiently strong to withstand", or "serviceable for use under" the pressure which is entered in the column headed  $P$ . In a few of these cases, moreover, the pressures referred to are not stated numerically in the articles cited, but have been supplied more or less satisfactorily from the context. These conjectural pressures are inclosed in parenthesis, and the corresponding value of  $PB/W$  is treated in the same way.

Each section of the table is arranged chronologically.

We are indebted to Mr. C. F. Hale, Wesleyan, 1903, for much assistance in the arrangement of this paper and for the drawings which it includes.

<sup>1</sup> Pogg. Ann. 46, 97-103 (1839). A tube of the same glass previously tested to 30 atm. burst after a time at 4 atm.

<sup>2</sup> Phil. Trans. 1845, 155-177; Ann. Chim. Phys. (3) 15, 257-290 (1845).

<sup>3</sup> Mechan. Mag. March 1849, No. 1337. Ref. Dingler, 112, 236 (1849). "Tubes of  $1\frac{1}{8}$ "- $2\frac{3}{4}$ " internal diameter and  $\frac{1}{11}$ "- $\frac{3}{16}$ " wall all withstood a pressure of 672 lbs. Two burst before 784. All the rest withstood 1568 lbs."

<sup>4</sup> Comptes rendus, 78, 411-413 (1874).

<sup>5</sup> Ref. Faraday, Chem. Manip., 1st Am. Ed., 1831, 397. The values of  $W$  and  $B$  are relative only. The pressure was 135 atm. of 14 lbs. each.

<sup>6</sup> Phil. Trans. 166, 421-449 (1876).

<sup>7</sup> Ber. chem. Ges. Berlin, 11, 818-822 (1878). 2 mm internal diameter and 3 mm wall, suitable for liquid chlorine at 148°. (2-3 mm wall and 1-4 mm internal diameter for liquid  $SO_2$  at the critical temperature. This is much too indefinite to tabulate. One extreme of choice would represent six times the strength of the other.)

<sup>8</sup> Comptes rendus, 90, 863-864 (1880).

<sup>9</sup> Chem. News, 41, 103-106 (1880).

<sup>10</sup> Comptes rendus, 101, 238-240 (1885).

<sup>11</sup> Ibid. 116, 1187-1189 (1893).

<sup>12</sup> Ibid. 133, 768-771 (1901). (a) Withstands for years the pressure of liquefied  $NH_3$ ,  $Cl$ ,  $H_2S$ . (b) For  $C_2H_2$  and  $HI$ .

<sup>13</sup> Ber. chem. Ges. Berlin, 36, 895-900 (1903).

Wesleyan University,  
Middletown, Conn.,  
July 27, 1903.



## NEW BOOKS

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**Vorlesungen über theoretische Physik.** By H. von Helmholtz. Band VI., *Theorie der Wärme.* Herausgegeben von Franz Richarz. Large octavo. pp. xii + 419. Leipzig: Johann Ambrosius Barth, 1903. Price: 16 marks.

— In view of the forbidding features for which the lectures of Helmholtz were famous, these ponderous books come to us with an agreeable surprise. Truly the *Notizbuch* of the Master and the *Collegienhefte* of his able pupil have been admirably *ausgearbeitet*, for there is little of the original abruptness left at which even the lazy student can take exception. When theta functions are advanced, for instance, the reader is given judicious but ample hints as to their purpose and treatment; and he soon agrees, complacently, that the very properties used were familiar. The reviewer at least confesses that the tremendous difference between doing a thing and contemplating the thing done has haunted him only as a disquieting afterthought; for the book is self-contained throughout.

In the first part of the volume, dealing with the analytical theory of heat and covering eight chapters in one hundred and twenty-five pages, there is small chance for any great novelty; and yet the reader is aware of not having come in contact with just this form of demonstration before. The early introduction of Green's theorem, a favorite with Helmholtz, and the vigorous use made of it to show that the solutions are necessarily unique, is not the customary procedure. Another feature is the very full treatment given to cylindrical conductors, an advantage certainly, since it is to these that the practical methods of Wiedeman and Franz, of Neumann, of Angström, and others, for measuring absolute or relative heat conductivity generally apply.

Naturally the discussion of terrestrial heat-conduction is very complete. Here Helmholtz was to some extent associated with Kelvin in reducing the age of our planet to the now well-known and much discussed limit of twenty-five to one hundred million years. Following both from Helmholtz's theory on the cause of solar heat, and from Kelvin's computation for the earth by a method which begins with present conditions and traces them back to the *consistentior status*, the argument has generally been regarded as trustworthy by physicists, with some marked exceptions, and it is strongly affirmed in the volume. The present era of radio-activity will certainly greatly modify Helmholtz's solar theory, and throw Kelvin's deductions back upon an inevitably precarious basis. That these theories have failed of the purposes for which they were written is now generally conceded.

The next section, on thermal radiation, is peculiarly interesting, not only for its terse treatment of the subject, but as an appreciative summary of the famous work of Kirchhoff, with whom Helmholtz was associated in Heidelberg and in Berlin throughout the greater part of his active life.

Thermodynamics is taken up in the second and by far the longest part of

the book, in which ninety-eight pages are devoted to the older and classical investigations and sixty-six pages to physical chemistry. The discussions relating to the first law are charmingly given, and might very well be used as a textbook of about the grade of Poincaré's *Thermodynamique*. Whatever accessory information the student needs is liberally dispensed. In order to accentuate the important bearing of the heat ratio of gases on the velocity of sound, for instance, a full discussion of the equations for aerial waves is inserted; and the illustrative chapter on the convective equilibrium of the atmosphere, a subject in which Helmholtz with Kelvin was much interested, subserves a similar purpose.

Quite different from this is the vigorous treatment of the second law, in which one at once becomes conscious of the guidance of a master. Of course the famous reasoning of Carnot inevitably predominates; but the early introduction of entropy-temperature coordinates and the rigor of the demonstrations is throughout worthy of Helmholtz.

The usual applications to fusion, evaporation, saturated vapors, etc., follow; and their important bearing on physical geology and meteorology is skillfully pointed out. The apologetic tone which Helmholtz takes in these chapters is frequently amusing, particularly as a contrast to the rigor of his logic. What can be more naive in so dignified a book than (to give a single instance), *So hängen die kleinen Veränderungen des Schmelzpunktes mit grossen und wichtigen Problemen zusammen*; to which one might add in parallel, "Great oaks from little acorns grow". The trouble is always to be quite sure that what one is planting is really an acorn and not a Yankee nutmeg. And again, when one recalls what sort of nutmeg came out of Connecticut, one cannot but agree that, in relation to thermodynamics at least, proverbs are sometimes misleading.

The next chapter, on thermodynamical potentials, will be read with especial interest because of Helmholtz's extensive original contributions to the subject. Helmholtz refers both the adiabatic and the isothermal potential unreservedly to Gibbs. One can but conjecture the bitter disappointment which Helmholtz must have felt on seeing the results of his eight years of labor so fully anticipated; but the text is without lamentation. The reviewer has always had the opinion that the intuitions of Massieu in propounding his *fonctions caractéristiques* were both precursory as well as independent. At least in his original papers Helmholtz acknowledges indebtedness to Massieu; and Gibbs in his discussion on the definition and properties of his fundamental equations makes a similar reference. Finally, with the great claimants to this powerful method of attacking thermodynamic problems, the name of Maxwell must be associated. Certainly no more lucid picture of the subject could be given than is contained in Maxwell's "available energy", announced as it was as an independent contribution if not as a prior claim.

Massieu's characteristic function for volume-temperature variables, when taken negatively, is Helmholtz's *freie Energie*; so that the former bears a relation to the latter similar to the work done by a body to its potential energy. Hence the work done by a system in a reversible isothermal transformation is the decrement of its *freie Energie*, and only such processes will spontaneously

occur in which this function decreases. At the very outset of his work, Helmholtz has thus corrected and interpreted Berthelot's law.

The great advantage of this method of computation is the ease with which it may be generalized to include any number of coordinates; and this is shown in the next section. Energy wherever met is given by an expression involving two distinct factors, and it is merely necessary to abstract from the immediate nature of these to marshal the whole subject analogically under a category of "forces" and "displacements". The expediency of introducing generalized coordinates at this stage of the investigation seems to the reviewer patent. In some books, largely of French origin, this is done at the beginning, and in contrast with the cumbersome equations which are dragged along the applications seem pitifully dilute.

The use made of his method in treating the theory of galvanic cells is somewhat sketchy, and does not read smoothly though it contains the gist of Helmholtz's great papers on the subject. The following chapter on the theory of solutions is also incomplete, inasmuch as, curiously enough, the name of van 't Hoff is not even mentioned. Helmholtz bases all his conclusions on the empiric law of vapor depression due to von Babo and Wüllner, with only a cursory reference to the work of Raoult. These gaps have to some extent been filled by the editor; but the scope of the deductions of the chapter are necessarily as restricted as the von Babo-Wüllner law which they contain.

The chapter which treats in turn of the usual subjects of the theory of solutions is none the less exceedingly interesting as a concrete example of the skill with which Helmholtz is able to apply his isothermal potential. Apart from technical difficulties, any other law than the one specified might be equally well inserted. The reader is impressed as if Helmholtz had a rigorous theory of solutions in view, of which the chapter recorded is a preliminary draft. Other parts of the book strike one in the same way.

The third volume of the book is a clear digest of Helmholtz's cycle theory. Heat is here treated as a case of cyclic motion, recalling in a measure Maxwell's deductions of the equations of the electromagnetic field from gyrostatic models. The justification of such an analogy is not at once evident; but out of the infinitude of infinitesimal lawlessness comes eventually the finite lawlessness of the heat phenomenon. Motion of a continuous medium in which the position abandoned by any particle is immediately reoccupied by another particle of the medium, in such a way, however, that relatively very gradual changes of path (slowly varying parameters) are not excluded, is what Helmholtz terms cyclic. The governor is a simple case with one parameter, the gyroscope another with two parameters. An excellent account of the theory in its magnetic applications is given in Ebert's *Kraftfelder*. Here we have Helmholtz's own account. For the reader's benefit all the relevant dynamics (Hamilton's and Lagrange's equations) are fully deduced. As a whole, the chapter is the most interesting in the book. Helmholtz succeeds in expressing the cyclical energy of a system as proportional to a function of its instantaneous condition, the factor being the cyclic velocity or, from another point of view, the kinetic cyclic energy. This result is in complete analogy with the heat temperature-entropy equation, and enables Helmholtz to interpret the second

law of thermodynamics, not as something merely peculiar to heat, but as a general deduction from the dynamics of cyclic systems. This accomplishment of Helmholtz has been variously discussed; but it is certain that nobody has come so near to giving the philosophical reason for the second law of thermodynamics.

The final section is a very brief exposition of the kinetic theory of gases. The treatment as a whole is elementary, Maxwell's distributive law being the only subject adequately dealt with; but even here the old and classic presentation of a straightforward case of probability is given. Naturally the vigorous recent discussions of the partitions of energy, due to Burbury, Jeans, and others, are not included; but one is disappointed not to find a more detailed account of Boltzmann's labors.

The reviewer closes this remarkable book with regret. A tone of philosophical candor pervades the whole of it. The mathematical style is not too severe, and the treatment preserves its refreshing originality throughout. In conclusion one cannot but congratulate Prof. Richarz for the ability with which he has accomplished what was doubtless a test of endurance. *Carl Barus*

**Elektro-Metallurgie.** *Die Gewinnung der Metalle unter Vermittlung des electrischen Stromes.* By W. Borchers. *Dritte vermehrte und völlig umgearbeitete Auflage; zweite abtheilung.* 16 X 24 cm; pp. viii + 584. Leipzig: S. Hirzel, 1903. Price: paper, 11 marks. — The first instalment of the third edition has already been reviewed (7, 218). This second portion completes the volume. The chapters on the Siemens and Halske process for extracting gold and on the Wohlwill process for refining gold have been rewritten so completely as to be practically new. Under silver there is an interesting account of an early attempt by Wohlwill to refine silver in a sulphate solution. Under zinc the work of Rontchewsky is new and there is an extended discussion of the Hoepfner process for making zinc and bleach. On the other hand, the cuts for the Borchers process of electrolyzing fused zinc chloride have disappeared.

Mennicke's work on tin is new; so is Salom's method of reducing galena; and Glaser's experiments on the precipitation of chromium from aqueous solutions were not to be found in the previous edition. Unfortunately the author has overlooked the new process of Betts for refining lead in a lead fluosilicate solution. The account of Keith's process is somewhat misleading in that Keith used a solution of lead sulphate in sodium acetate and not a lead acetate solution.

The chapter on the production of steel in the electric furnace is practically new, and the chapter on carbides is much changed from the previous edition. It is to be regretted that the Horry furnace is mentioned only in a footnote as one of a series of revolving furnaces. From the book one would imagine that this was a foolish invention which was mentioned merely for the sake of completeness. No one would ever suspect that all the carbide manufactured in the United States is made in a revolving furnace. Another instance of the ignoring of actual facts is to be found in the comparison between the Siemens-Halske and the McArthur-Forrest processes. Borchers quotes from a book published in 1895, and states that zinc precipitation cannot compete with electrolytic.

The facts are that the precipitation by zinc is holding its own very well in South Africa and that it has the whole field in this country. This may be due to conservative and ignorance; but one would have preferred a discussion of the matter to an *ex cathedra* statement based on data which no longer apply.

Wilder D. Bancroft

**Electrolytic Preparations.** By Karl Elbs. Translated by R. S. Hutton. 14 × 22 cm; pp. xi + 100. London: Edward Arnold; New York: Longmans, Green and Co., 1903. Price: bound, \$1.60, net. — The original German edition has already been reviewed (6, 270). It is a pleasure to note the appearance of an English translation of this excellent work. The translation has been well done.

Wilder D. Bancroft

**Vorlesungen über theoretische und physikalische Chemie.** By J. H. van't Hoff. Drittes Heft: Beziehungen zwischen Eigenschaften und Zusammensetzung. Zweite Auflage. 15 × 23 cm; pp. x + 155. Braunschweig: F. Vieweg und Sohn, 1903. Price: paper, 4 marks. — The new edition contains about ten pages more than the old. The increase is due to the addition of a few lines here and a paragraph there. To quote the term applied to another of the author's books it is evident that this one is to be looked upon as a "document". The work reached its definitive form and scope in the first edition, and subsequent editions are to preserve these characteristics practically unchanged.

Wilder D. Bancroft

**Journal de chimie physique.** Edited by P. A. Guye. 16 × 25 cm. Geneva: Henry Kundig. Paris: Gauthier-Villars. — We welcome the appearance of a French magazine devoted to physical chemistry which will undoubtedly do much to develop physical chemistry in France. There are some who believe that we are drifting in the direction of a universal scientific language which is to be either German or English, presumably German. If these people are right, M. Guye is wrong in starting his publication. Those, who take a wider and a clearer view of existing facts and prevailing tendencies, have long since realized that the most vital thing to-day is the spirit of nationality and that the best results for the individual scientific man and for the scientific world as a whole is for each man to do his utmost to develop science in the land where he lives. We may study under and, later, collaborate with German scientific men, but an American scientific man is an American and will remain one. It is merely self-delusion to classify himself as a cosmopolite. He harms himself and, which is more serious, he harms his science. The same reasoning applies to the French-speaking people as to the English-speaking people, and therefore M. Guye is right in starting his journal and we wish him the success which is his due.

Wilder D. Bancroft

**Die Konstitution des Kamphers und seiner wichtigsten Derivate.** Die theoretischen Ergebnisse der Kampherforschung. By Ossian Aschan. 14 × 23 cm; pp. ix + 117. Braunschweig: Friedrich Vieweg und Sohn, 1903. Price: paper, 3 50 marks. — After a short historical preface, the author enumerates thirty-three different structural formulas for camphor which at one time or other have found adherents; and gives in most cases the reasons that led to their introduction.

Twelve theses are then defended — camphor is a ketone, camphor contains the group  $\text{—CH}_2\text{CO—}$ , etc., etc., — and finally the thirty-three formulas are compared with the twelve theses, and only one of the former found to be in accord with all of the latter.

The formula so arrived at, the now generally accepted formula of Bredt, explains “for the most part in a clear and elegant manner” all the reactions of camphor, and is moreover in accord with the generalizations which connect heat of combustion, refractive index, and optical rotation, with the constitution of organic compounds.

The closing chapters are devoted to an account of reactions which have not proved useful in fixing the constitution of camphor, and in regard to some of which opinions are still divided.

The book is clearly written and well arranged, and as all laboratory details are omitted and nothing but results recorded, it offers in small compass a welcome synopsis of the very numerous investigations in this important group.

W. Lash Miller

*Theorie der Bewegungsübertragung, als Versuch einer neuen Grundlegung der Mechanik.* By Richard Manno. 16 × 24 cm; pp. 102. Leipzig: Wilhelm Engelmann, 1903. Price: paper, 2.40 marks. — In place of regarding force as the cause of motion, or, contrariwise, of defining and measuring force by the observed effect, the author of this pamphlet has endeavored to construct a system of mechanics in which force is regarded as the phenomenon of motion itself. Apparently he has been led to this attempt by a conviction that all the terms used in an exposition of mechanics should represent observable phenomena. In order to get rid of the idea of action at a distance, he supposes every force to be due to impact, regarding motion as transferred from body to body by a succession of intervening impacts.

J. E. Trevor

## REVIEWS

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*The object of this department of the Journal is to issue, as promptly as possible critical digests of all Journal articles that bear upon any phase of Physical Chemistry*

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### General

**Revision of the atomic weight of caesium.** *T. W. Richards and E. H. Archibald. Proc. Am. Acad.* 38, 443; *Zeit. anorg. Chem.* 34, 353 (1903). — Analyses were made of caesium chloride, caesium bromide and caesium nitrate, the last by heating with sand. The most probable value for the atomic weight of caesium is 132.879. In checking this result, values of 39.14 for potassium and 14.04 for nitrogen were obtained. *W. D. B.*

**The atomic weight of fluorine.** *J. Meyer. Zeit. anorg. Chem.* 36, 312 (1903). — Calcium oxide was converted into calcium fluoride. Taking the atomic weight of calcium as 40.136, the most probable value for fluorine is 19.036. *W. D. B.*

**The atomic weight of lanthanum.** *H. C. Jones. Zeit. anorg. Chem.* 36, 92 (1903). — In this reply to Brauner (7, 222) it is pointed out that lanthanum oxide becomes discolored when heated in a platinum crucible by the method of Brauner, while it remains white when heated in a porcelain crucible. This discoloration is due to an oxidation and is believed to account for the difference between the determinations of Brauner and of Jones. *W. D. B.*

**Continuous electrical calorimetry.** *H. L. Callendar. Phil. Trans.* 199A, 55 (1902). — A discussion in detail of the author's method of continuous flow calorimetry. The paper is divided into five parts: introduction, electrical measurements, electrical thermometry, calorimetry, discussion of results. *W. D. B.*

**On the capacity for heat of water between the freezing- and boiling-points together with a determination of the mechanical equivalent of heat in terms of the international electric units.** *H. T. Barnes. Phil. Trans.* 199A, 149 (1902). — The method was the one devised by Callendar (preceding review). The investigation is a marvel of painstaking accuracy, and the results are unquestionably the most accurate ever obtained, in spite of the fact that there is an unexplained discrepancy between the author's results and those of Griffiths and of Schuster and Gannon. The following table gives the absolute value of the thermal capacity of water in joules per calorie for different temperatures expressed in terms of the Clark cell as 1.43325 int-volts at 15° and of the ohm as 1.01358 B. A. units :

Temp.	Joules	Temp.	Joules	Temp.	Joules
5°	4.2050	35°	4.1718	65°	4.1815
10	4.1924	40	4.1718	70	4.1843
15	4.1840	45	4.1727	75	4.1870
20	4.1783	50	4.1743	80	4.1899
25	4.1746	55	4.1764	85	4.1927
30	4.1725	60	4.1790	90	4.1955
				95	4.1983

The mean value over the whole range is 4.18326, agreeing very closely with Reynolds and Moorby's value of 4.18320. No physical significance can be assigned to the minimum specific heat at about 37°.

W. D. B.

**Animal thermostat.** *Lord Kelvin. Phil. Mag.* [6] 5, 198 (1903).—The fact that the animal body is maintained at a constant temperature when in a surrounding medium, either above or below it in temperature, forms the subject of discussion. It is pointed out that the production of cold in the body calls for more extended experiment. The early experiments of Crawford in 1781 are discussed in this connection.

H. T. B.

#### One-Component Systems

**On bismuth oxide.** *W. Guertler. Zeit. anorg. Chem.* 37, 222 (1903).—When bismuth oxide is melted (in a platinum crucible?), it begins to freeze at 820° and its first modification changes to a second at 705°. When a porcelain crucible was used, it was attacked and a third modification separated at 860°, which was stable at all temperatures. The density of the second modification is  $8.20 \pm 0.10$ , and of the third is  $8.55 \pm 0.05$ . The change of the first modification into the second at 705° is accompanied by an emission of light.

W. D. B.

**An experiment on critical density.** *J. Traube. Zeit. Elektrochemie*, 9, 619 (1903).—The author shows that differences of density can exist in a tube in which a liquid has been heated above the critical temperature. From this he deduces the existence of liquid molecules and gas molecules which become miscible in all proportions at the critical temperature. Since the compressibility is great at the critical temperature, and since any impurity affects the results enormously, these conclusions will not be accepted until it is proved that the liquid was absolutely pure and that there were no pressure differences in the tube. In view of the great difficulty in getting any substance absolutely pure, it seems more reasonable to refer the phenomenon to this, as has been done by others. The rate of heating might also have an effect if the liquid were polymerized at the critical temperature. It is even more probable that the temperature was not uniform inside the tube.

W. D. B.

**On the measurement of temperature.** *M. W. Travers, G. Senter, and A. Jaquerod. Phil. Trans.* 200A, 105; *Zeit. phys. Chem.* 45, 385, 416, 435 (1903).—This paper is divided into three parts, the first dealing with the pressure coefficients of hydrogen and helium at constant volume and at different initial pressures; the second with the vapor-pressures of liquid oxygen at temperatures below its boiling-point on the constant-volume hydrogen and helium scales; the third with the vapor-pressures of liquid hydrogen at temperatures below its boiling-point on the constant-volume hydrogen and helium scales.



The value for the pressure coefficient of hydrogen at an initial pressure of 500 mm is 0.0036627 and for helium 0.0036625 and 0.0036631. When Chappuis's measurements on the pressure coefficients of nitrogen are extrapolated for zero pressure, the value lies between 0.003662 and 0.003663. Assuming "that the pressure coefficient for hydrogen and helium is 0.00366255 and is independent of the pressure below 1000 mm of mercury, it is probable that the melting-point of ice on the absolute scale does not lie very far from 273.03°."

The vapor-pressure of liquid oxygen is 150 mm at 77.17° on the helium scale and 800 mm at 90.70° on the same scale. The boiling-point under 760 mm pressure is 90.20° on the helium scale. "At an initial pressure of one meter of mercury at the melting-point of ice, the constant-volume hydrogen and helium scales differ by 0.1 at the boiling-point of liquid oxygen," the temperature on the hydrogen scale being lower. Since the critical temperature of hydrogen is about 35° abs and that of helium about 10° abs, it is probable that the helium scale is more nearly right than the hydrogen scale.

The vapor-pressures of liquid hydrogen are 50, 100, 300, 600, 760 and 800 mm at 14.11°, 15.14°, 17.57°, 19.61°, 20.41°, and 20.60°, respectively, on the helium scale. On the hydrogen scale the values from 100 to 800 mm are about 0.2° lower. The melting-point of hydrogen is 14.1° on the helium scale, the pressure being 49-50 mm. Solid neon has a vapor-pressure which does not change as the substance evaporates. It is therefore probably homogeneous. The observed vapor-pressure was 2.4 mm at 15.65° He and 12.8 mm at 20.4° He.

From the critical and boiling-points of krypton and neon the authors conclude that the critical point for helium should be about 10° abs and the boiling-point about 6° abs. Special experiments were made to liquefy helium and a temperature of about 13° abs was reached, but the helium showed no sign of liquefaction. The authors recommend that the Joule-Thomson effect for helium should be determined over a wide range of temperatures. *W. D. B.*

The specific heats of metals and the relation of specific heat to atomic weight, II. *W. A. Tilden. Phil. Trans. 201A, 37 (1903).*—The specific heats of aluminum, nickel, silver, and platinum have been determined from 100° abs to 700° abs, and with platinum up to 1400° abs. The specific heats vary as follows between 100° abs and 700° abs: Al, 0.1226-0.2531; Ni, 0.0575-0.1301; Ag, 0.0467-0.0590; Pt, 0.0275-0.0372. From an extrapolation for the atomic heats of silver and platinum, it is probable that these do not meet at the absolute zero. With the four metals studied, the temperature coefficient of the specific heat is greater, the lower the atomic weight. *W. D. B.*

On quartz glass. *H. Heraeus. Zeit. Elektrochemie, 9, 847 (1903).*—Rock crystals change to glass at about 1700°. At 1500° the glass is distinctly plastic, but the temperature at which it can really be worked is above 2000°. At 2300°-2400° the glass vaporizes fairly rapidly. A quartz tube should not be touched by the hands after having been cleaned and before being heated; otherwise spots of alkali silicate will be formed. When heated in a porcelain tube to 1300°, the tube becomes opaque on the surface, due to vaporization of alkali from the porcelain. When quartz is heated in the air oxides of nitrogen are formed in perceptible quantity. Since the ultra-violet rays pass readily through quartz, much ozone is formed when an Arons mercury lamp is made with quartz instead of glass. *W. D. B.*

*Two-Component Systems*

**On the constitution of the copper-tin series of alloys.** *C. T. Heycock and F. H. Neville. Phil. Trans. 202A, 1 (1903).* — The substance of this paper was published in outline some time ago (6, 498), and we now have all the details with 101 micro-photographs. The phases in equilibrium with the melt are:  $\alpha$ -crystals, containing 0.9 percent tin;  $\beta$ -crystals, containing 22.5–27 percent tin;  $\gamma$ -crystals, containing 28.57 percent tin;  $\text{Cu}_3\text{Sn}$ ;  $\text{CuSn}$ ?; pure tin. The evidence in favor of  $\text{CuSn}$  is not looked upon by the authors as conclusive. All that can be said is that this is pretty nearly the composition of the phase. Both the analyses and the microscopical structure would fit in better with the assumption of  $\text{Cu}_3\text{Sn}_2$ . In addition to these solid phases, there is another,  $\text{Cu}_3\text{Sn}$ , which is formed at lower temperatures by the breaking down of the  $\beta$ - and the  $\gamma$ -crystals.  
W. D. B.

**On the alloys of mercury.** *N. A. Puschin. Zeit. anorg. Chem. 36, 201 (1903).* — The author has studied the freezing-point curves, the electromotive forces and the microscopic structure of a number of amalgams. The evidence is pretty strongly in favor of the view that zinc, bismuth, lead, tin, and copper form neither compounds nor solid solutions with mercury, while cadmium forms two series of solid solutions.  
W. D. B.

**On the connection between freezing-points, boiling-points and solubilities.** *M. Wildermann. Phil. Mag. [6] 5, 405 (1903).* — The author shows that the determination of the points of intersection of the freezing-point and boiling-point curves with the solubility curve, which gives the freezing-point and boiling-point of the saturated solution in the presence of an excess of the dissolved substance, renders it possible to connect solubility, freezing- and boiling-point curves, the latent heats of melting and of solution, and the latent heat of evaporation, and to calculate solubilities from freezing-points and boiling-points.

The equations connecting the different phenomena are derived from van't Hoff's thermodynamic equations. It is suggested that it may be possible to disclose some new thermodynamic connections by means of reversible cycles. Such a cycle would extend along a freezing-point curve, then along the curve of pure water or of an unsaturated solution, then along the boiling-point curve back to the starting-point. A diagram showing the vapor-pressures at different temperatures is given in illustration.  
H. T. B.

**Bibliography of metallic alloys.** *M. Sack. Zeit. anorg. Chem. 35, 249 (1903).* — The papers with the alloys studied are arranged in an alphabetical list of authors. A special alphabetical list of metals gives page references to the first list. The author must have spent a good deal of time in preparing this bibliography, for it is a most excellent one. It will be of immense service to those interested in alloys.  
W. D. B.

*Multi-Component Systems*

**The reduction of metallic oxides by hydrogen.** *F. Glaser. Zeit. anorg. Chem. 36, 1 (1903).* — In the system  $2\text{Ag}_2\text{O} + \text{H}_2 = \text{Ag}_4\text{O} + \text{H}_2\text{O}$  we have three components and three phases. If we work at constant atmospheric pressure,

there is but one temperature at which these three phases can co-exist in stable equilibrium. Putting it another way, there must be a definite temperature at which  $\text{Ag}_2\text{O}$  begins to be reduced by a current of hydrogen. The author has determined these temperatures for a number of oxides. The temperatures, at which the following substances are formed, are :  $\text{Ag}_2\text{O}$ ,  $34^\circ$  ;  $\text{Ag}$ ,  $63^\circ$  ;  $\text{Hg}$ ,  $75^\circ$  from the yellow oxide and  $140^\circ$  from the red ;  $\text{PbO}$ ,  $189^\circ$  ;  $\text{Pb}_2\text{O}$ ,  $211^\circ$  ;  $\text{Pb}$ ,  $235^\circ$  ;  $\text{Cd}$ ,  $282^\circ$  ;  $\text{Ni}_3\text{O}_4$ ,  $188^\circ$  ;  $\text{NiO}$ ,  $198^\circ$  ;  $\text{Ni}_2\text{O}$ ,  $230^\circ$  ;  $\text{NiO}$ ,  $339^\circ$  ;  $\text{Co}_3\text{O}_4$ ,  $182^\circ$  ;  $\text{CoO}$ ,  $207^\circ$  ;  $\text{Co}$ ,  $228^\circ$  ;  $\text{Fe}_2\text{O}_4$ ,  $287^\circ$  ;  $\text{FeO}$ ,  $305^\circ$  ;  $\text{Fe}$  about  $370^\circ$ . With a mixture of two metallic oxides, it is obviously possible to reduce one to the metal and then the other, giving a quantitative analysis with a double determination. The extraordinary thing about these experiments is the formation of water at  $34^\circ$  in the case of silver oxide. Special experiments seemed to show that silver and silver oxide were not catalytic agents. The author expresses an opinion that the silver oxides may give off "atomic" oxygen instead of "molecular" oxygen.

W. D. B.

**On complex mercury halides.** *M. S. Sherrill. Zeit. Electrochemie*, 9, 549 (1903). — Reviewed (7, 545) from *Zeit. phys. Chem.* 43, 705 (1903).

**Absorption, VIII ; absorption compounds of hydrogels when chemical compounds or solutions can occur.** *J. M. van Bemmelen. Zeit. anorg. Chem.* 36, 380 (1903). — In this paper the author presents experiments on three types. The first is that in which a substance precipitates a hydrosol and is absorbed by the resulting gel. This is realized with barium hydroxide and ferric oxide. The second type is that in which the gel and the absorbed substance can finally form a solution. This is to be found with strong acids and the ferric oxide hydrosol. The last case is that in which a definite chemical compound is formed. This occurs with barium hydroxide and the silicic acid hydrosol.

The amount of barium hydroxide absorbed by the ferric oxide gel increases rapidly at first with increasing concentration of solution ; but this rate soon falls off approximately to zero. Barium chloride is also absorbed. On standing, barium chloride diffuses back into the solution, but at the same time much more barium hydroxide diffuses from the solution into the gel. Acids precipitate a ferric oxide gel and are absorbed by it. On standing, however, the gel redissolves, most rapidly in hydrochloric acid, less rapidly in nitric acid, and least rapidly in sulphuric acid.

When barium hydroxide is added to a silicic acid hydrosol in a ratio of less than 0.5 mol  $\text{BaO}_2\text{H}_2$  to 1.0 mol  $\text{SiO}_2$ , a gel is formed which contains barium hydroxide, but which shows no sign of crystallization. With more barium hydroxide crystals appear. With an excess of barium hydroxide the gel changes soon to crystallized  $\text{BaSiO}_3\cdot 6\text{H}_2\text{O}$ , a salt which dehydrates at constant vapor pressure to  $\text{BaSiO}_3\cdot \text{H}_2\text{O}$ .

W. D. B.

**On silicic acid.** *E. Jordis. Zeit. anorg. Chem.* 34, 455 ; 35, 16 (1903). — Purified silicic acid was dissolved in a dilute warm  $\text{NaOH}$  solution so that the ratio of sodium to silica was unity. From this sodium silicate, silicic acid was precipitated. It cannot be freed completely from alkali unless hydrochloric acid is added in excess during the dialysis. Testing the liquid that has passed through the membrane is extremely inaccurate and the silicic acid solution

must itself be tested. This 'pure' silicic acid is extremely insoluble but dissolves readily in presence of small amounts of alkali, acid or organic substances.

W. D. B.

On the silicates, I.-III. *E. Jordis and E. H. Kanter. Zeit. anorg. Chem.* 35, 82, 148, 336 (1903). — From measurements of the conductivity of solutions of silicic acid to which ammonia is added in varying amounts, the authors satisfy themselves of the existence in solution of a mono-ammonium and a di-ammonium silicate. It is quite conceivable that this conclusion may be vitiated by experimental error.

The authors study the behavior of the silicates of the alkaline earths in presence of water, and are much puzzled because the ratio of acid to alkali in the solution is not the same as in the solid phase. In fact, the authors are hopelessly handicapped by their ignorance of the phase rule, as will be seen very clearly by comparing their work with that of van Bemmelen. W. D. B.

The precipitation of crystalline gold by formaldehyde. *N. Averkieff. Zeit. anorg. Chem.* 35, 329 (1903). — While most reducing agents precipitate gold in an apparently amorphous state, formaldehyde precipitates it in visible crystals from a concentrated strongly acid gold solution. The density of this gold at 20° is 19.43, much higher than any value previously obtained.

W. D. B.

On the combustion of carbon in the calcium carbide reductions. *B. Neumann. Zeit. Electrochemie*, 9, 699 (1903). — Another reply to v. Kügelgen (7, 546).

W. D. B.

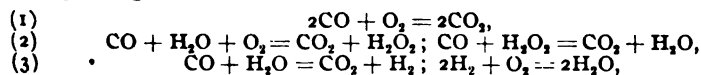
#### Velocities

Contribution to the kinetics of the reaction between carbon monoxide and oxygen. *H. Kühl. Zeit. phys. Chem.* 44, 385 (1903). — The measurements were carried out in the hope of throwing light on the remarkable influence exerted by traces of water vapor on the rates of many reactions between gases.

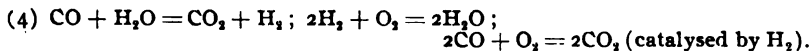
The gases were heated to 570° in glazed porcelain vessels, the progress of the reaction being followed manometrically. The thermostat, thermometer, gasometers, etc., are described in full.

The rate is roughly proportional to the concentration of the carbon monoxide, and it is to a great extent independent of that of the oxygen; it increases irregularly with increase in the amount of water vapor, and is retarded by carbon dioxide. The rate is in the highest degree dependent on the order in which the gases are introduced into the porcelain vessel; this fact and many others brought out in the course of the investigation are ascribed to the influence of the walls of the vessel in which the reaction was carried out.

The experiments could not be brought into accord with the kinetic equations corresponding to the reactions:



but an empirically discovered differential equation, which reproduces the experiments fairly well, is of the same form as the kinetic equation deduced from the following assumptions as to the mechanism of the reaction:



Nothing of the nature of Hélier's "false equilibria" could be discovered. As appendix, the author gives an integral form of the equation

$$dx/dt = k(a-x)(b-x)^2$$

suitable for use when  $a$  is nearly equal to  $b$ .

W. L. M.

On the rate of change of persulphuric acid into Caro's acid and on the formula of the latter. *M. Mugdan. Zeit. Elektrochemie*, 9, 719 (1903).—The rate of change of persulphuric acid into Caro's acid can be expressed quite accurately by the equation for a mono-molecular reaction. The formula for Caro's acid is apparently  $\text{H}_2\text{S}_2\text{O}_8$ .

W. D. B.

Studies in technical processes. *G. Bodländer and K. Köppen. Zeit. Elektrochemie*, 9, 559, 787 (1903).—In the first paper the authors study the reaction velocity in the contact sulphuric acid process. The reaction seems to be one of the third order, but this is not certain because the "constant" varies with the relative amounts of  $\text{SO}_2$  and  $\text{O}_2$ , also with the presence of nitrogen. Asbestos cannot be used as a support for the platinum because it is attacked by the sulphur trioxide. In the reaction velocity experiments, massive platinum netting was used as catalytic agent.

In the second paper the authors study the equilibrium relations by the static method, using a quartz tube. At high temperatures the platinum was apparently oxidized by the oxygen. The equilibrium constant is independent of the relative masses of the reacting gases and is not affected by the presence in a vessel of so-called indifferent gases. A table is given showing the yield of  $\text{SO}_3$  at different temperatures for different initial relative concentrations. When diluted with air, the system can be heated to a higher temperature and still give the same yield. As the reaction velocity is much greater the higher the temperature, it is commercially advantageous to work with diluted gases.

W. D. B.

The hydrolysis of the trisaccharides by dilute acids. *A. Wogrinz. Zeit. phys. Chem.* 44, 571 (1903).—As the author was unable to bring his measurements to a conclusion, he seeks to "reserve" this department of research by publishing a set of kinetic equations.

W. L. M.

On the movements of the flame in the explosion of gases. *H. B. Dixon. Phil. Trans.* 200A, 315 (1903).—The detonation waves and their reflections have been analyzed photographically by means of a film on the circumference of a rapidly rotating wheel. By means of by-passes and double tubes, it was possible to produce all sorts of changes, such as having a sound-wave meet or follow a detonation-wave, or having two detonation-waves meet end-on. Where two tubes are joined together, disturbances occur if the joint is not absolutely rigid. For a long time the importance of this was not appreciated.

In an exploded mixture of  $\text{C}_2\text{N}_2$  and  $\text{O}_2$  the velocity of the first sound-wave was 1116 m/sec, of the second 1014 m/sec, and of the third 893 m/sec. When two detonation-waves meet in collision the gases are more luminous than when the wave strikes a flat piece of metal at the end of the tube. The reflected wave has a higher velocity in the first case than in the second.

The detonation-wave always starts with an abrupt spring. Sometimes there is only one abrupt change and sometimes several abrupt changes occur in the acceleration before the final spring which marks the detonation-wave. Each of these abrupt changes is always accompanied by a luminous wave thrown back from the ignited gases. This wave the author calls the retonation-wave. The dark space formed where the detonation and the retonation-waves originate is undoubtedly a space of cooler gas.

In 1900 Le Chatelier put forward the view that the wave of detonation starts in front of the variable wave (which is increasing in velocity), and originates in an invisible wave, which is proceeding in front of the visible wave and with a velocity equal to it. Special experiments were made which apparently disprove the existence of Le Chatelier's "invisible wave". Still other experiments showed the incorrectness of the view of v. Oettingen and v. Gernet "that the detonation of electrolytic gas is invisible and that the salts present in their experiments only became luminous after the combustion had been for some time complete.

There are eighty-two cuts illustrating the article, most of them photographs.

W. D. B.

#### *Electromotive Forces*

**Removal of the volta potential difference by heating in oil.** *J. Brown. Phil. Mag.* [6], 5, 591 (1903).—The author revives the question of the cause of the volta potential by bringing forward an experiment, which demonstrates the seat of the action to be condensed films on the surface. Plates of copper and zinc are immersed in heavy petroleum oil, and heated to 145° C. The volta effect disappears at that temperature and remains absent after the oil has cooled. The conclusion is reached that the moisture of the air, existing as a film on the surface, causes the potential difference.

H. T. B.

**Calculation of the electromotive force of two opposed cells of the calomel type.** *J. N. Brønsted. Zeit. anorg. Chem.* 37, 158 (1903).—The author shows that the formula, usually given for the electromotive force of concentration cells without diffusion, is not general; but contains the assumption that the ion is monatomic. At the time the formula was deduced the possibility of anything else never occurred to anybody. With mercurous nitrate we could have such a case and possibly with cuprous chloride. The author deduces the general formula, but without reference to mercurous nitrate or cuprous chloride.

W. D. B.

**On the thallium accumulator.** *L. Jones. Zeit. Elektrochemie*, 9, 523 (1903).—The thallium oxide which precipitates at the anode appears to have the formula  $3\text{Tl}_2\text{O}_3 \cdot \text{Tl}_2\text{O}_4$ . The electromotive force of thallium concentration cells was studied and the results indicated that the oxide was really  $\text{Tl}_2\text{O}_3$ .

W. D. B.

**The formation and significance of sodium alloys with cathodic polarization.** *M. Sack. Zeit. anorg. Chem.* 34, 286 (1903).—When lead and tin cathodes are highly polarized in caustic soda solutions, the evolution of hydrogen is accompanied by a disintegration of the metal due to the formation of a rich

sodium alloy, which decomposes in this way with water. The surface becomes rough when the potential against hydrogen in the same caustic soda is 0.7 volt for lead, 0.4 volt for tin. The rapid disintegration takes place at a potential of 1.5 volts for lead and 1.4 volts for tin, both measured against hydrogen in the same solution as zero. Zinc and platinum become rough but do not disintegrate in clouds. Since hydrogen dissolves in platinum more readily than does sodium, a platinum surface becomes rough more rapidly in acid solutions than in alkaline. Measurements of potentials of sodium alloys in a methyl alcoholic solution of lithium chloride at  $-80^{\circ}$  showed that a surface layer of the nobler metal formed whenever the nobler metal was present as phase. *W. D. B.*

On anode potentials during the formation of lead carbonate and chromate. *G. Just. Zeit. Elektrochemie*, 9, 547 (1903). — With lead in sodium chlorate solution we get the anode potential of pure lead. When sodium carbonate is added in increasing amounts, the anode potential varies continuously from that of pure lead to that of lead peroxide. A similar phenomenon was observed with sodium chromate, the change taking place at lower concentrations for the chromate than for the carbonate. *W. D. B.*

On standard electrochemical units. *W. Nernst. Zeit. Elektrochemie*, 9, 685 (1903). — A list of abbreviations recommended by the German Bunsen Society. *W. D. B.*

On a new electric resistance furnace. *O. Fröhlich. Zeit. Elektrochemie*, 9, 628 (1903). — The author has constructed a resistance furnace in which the heating coils are made of a substance analogous to that in the Nernst lamp; but differing from it in that it conducts at low temperatures. The objection to using Nernst glowers in constructing a furnace has been the extreme brittleness of the mass. If the author has succeeded in eliminating these difficulties, it will be a great thing. The platinum foil furnaces of Heraeus are excellent, but they do break down in time. *W. D. B.*

The thermomagnetic and related properties of crystalline bismuth. *L. Lownds. Phil. Mag.* [6], 5, 141 (1903). — The author continues his work (6, 157) on the thermomagnetic and thermoelectric properties of a special plate of crystallized bismuth. The present paper contains the change of the electrical resistance in the magnetic field, the Hall effect, and the change in the thermal conductivity produced by a strong magnetic field. The conductivity in two directions, along and at right angles to the chief crystallographic axis, is determined. *H. T. B.*

#### *Electrolysis and Electrolytic Dissociation*

Efficiency of the nickel-plating tank. *O. W. Brown. Trans. Am. Electrochem. Soc.* 4, 83 (1903). — With cast nickel anodes in ammonium nickel sulphate the anode efficiency was 91.3 percent and the cathode efficiency 92.1 percent when the surface of the anodes was roughened in acid. When the surface was ground smooth, the anode efficiency was 46.3 percent and the cathode efficiency 75.4 percent. With a pure rolled anode the anode efficiency was 8.5 percent and the cathode efficiency 63.3 percent. With anodes of electrolytic nickel the efficiencies are 12.7 percent and 61.6 percent respectively. The

cathode efficiency therefore decreases with decreasing anode efficiency. The slightly impure cast anodes dissolve much more readily than the less porous pure anodes, while the increase of surface, caused by roughening with acid, has a very marked effect.

W. D. B.

Contributions to our knowledge of ozone. *L. Gräfenberg. Zeit. anorg. Chem.* 36, 355 (1903). — By electrolysis of hydrofluoric acid under suitable conditions an oxygen can be obtained which contains five percent of ozone. This much can however be obtained with less trouble by electrolyzing sulphuric acid. A ten percent ozone gives a potential difference of 1.65 against hydrogen. The author believes that an ozone electrode is to be considered as one reversible with reference to hydroxyl as ion. In support of this view he cites evidence in favor of the existence of an ozone acid,  $H_2O_4$ , in solution.

W. D. B.

The effect of the nature of the electrolyte and the electrode on the formation of ozone. *R. Kremann. Zeit. anorg. Chem.* 36, 403 (1903). — More ozone is formed in sulphuric acid solutions when lead peroxide points are used than with platinum points. Increasing the surface of the electrode decreases the yield, the current density remaining constant. [This is probably the result of heating and could be avoided by cooling the electrode instead of the electrolyte.] Sulphuric acid is a better electrolyte than chromic acid or phosphoric acid. With platinum points in caustic potash, measurable quantities of ozone are obtained only at very low temperatures.

W. D. B.

Historical data on the electrolytic formation of hydrogen peroxide. *F. Richarz. Zeit. anorg. Chem.* 37, 75 (1903). — The author points out that Bornemann (7, 486) has mis-stated several facts in regard to the earlier work on the electrolytic formation of hydrogen peroxide.

W. D. B.

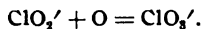
A new type of electrolytic cell. *P. G. Salom. Trans. Am. Electrochem. Soc.* 4, 100 (1903). — The difficulty with the Salom process has been the incomplete reduction of the ore. By using a layer of ore only one-tenth of an inch thick a satisfactory reduction could be obtained with a high current efficiency. This would however require fifty thousand cells to give an output of ten tons of lead per day. The current has therefore been increased from 12 amp/sq. ft. and 1 amp/lb to 30 amp/sq. ft. and 50 amp/lb. While the current efficiency is only 66 percent, the contents of the cell are reduced and removed every revolution of 1.5 hours instead of every five days. With 100 cells it will be possible to produce ten tons of lead per day.

W. D. B.

On electrolytic formation of perchlorates. *W. Oechsli. Zeit. Elektrochemie*, 9, 807 (1903). — It seems probable that the formation of perchlorate is due to the interaction of chlorate as ion according to the equation



The chlorite as ion is oxidized by electrolytic oxygen to chlorate



In alkaline solution hydroxyl is set free at the anode instead of chlorate and little perchlorate is formed. In neutral solutions, especially at higher temperatures, oxygen may easily be evolved from the primary decomposition of water. We therefore get a low temperature and a slightly acid solution as absolutely



necessary, also a high concentration. A high current density is desirable but not essential. The author has been very careful in following out the details of the problem and has paid especial attention to the chemistry of the reaction.

W. D. B.

**The electrolysis of the alkali sulphides.** *A. Brochet and G. Ranson. Zeit. Elektrochemie*, 9, 509, 531 (1903). — When an alkali sulphide solution is electrolyzed at 50°, sulphur is set free, which dissolves as a polysulphide and is reduced by the hydrogen at the cathode to hydrogen sulphide. The authors have studied the reaction with and without a diaphragm. With barium sulphide, barium hydroxide can of course be obtained by using a diaphragm.

W. D. B.

**The electrochemistry of the iodine oxygen compounds.** *E. Müller. Zeit. Elektrochemie*, 9, 584, 707 (1903). — There is first a repetition of Luther's views on the equilibrium between metallic, univalent and bivalent copper. Then these views are applied to the oxygen-iodine compounds and are tested by electromotive force measurements with alkaline iodide, iodate and periodate solutions. There is a qualitative but no quantitative agreement with Luther's conclusions. From the measurements, the author deduces that potassium iodide and potassium periodate must react to form potassium iodate, which proves however not to be the case in alkaline solution. Under the influence of heat, light, platinum or acids as catalytic agents, the reaction takes place.

W. D. B.

**A practical utilization of the passive state of iron.** *C. F. Burgess. Trans. Am. Electrochem. Soc.* 4, 31 (1903). — Before a steel bicycle frame can be enamelled, it is necessary to remove the brass left after brazing the joints. This can be done electrolytically by making the frame anode in a sodium nitrate solution. Special experiments showed that the potential of the iron became approximately that of the peroxide plate in the lead storage battery.

W. D. B.

**Electrolysis with alternating currents.** *M. Le Blanc. Zeit. Elektrochemie*, 9, 636 (1903). — It has been stated by J. W. Richards (7, 324) that cadmium sulphide can be prepared by passing an alternating current through a sodium hyposulphite solution, using cadmium electrodes. The author has repeated these experiments and finds that the yield is very small with 1000 alternations per minute. It increases with decreasing alternations and with increased stirring. Experiments were then made on the behavior of copper electrodes in potassium cyanide solution as it was believed that this might give an approximate idea of the rate of formation of the complex salt. Here again the yield decreases with increasing rate of alternation; but not so rapidly as in the case of the cadmium electrodes in the hyposulphite solution. In 4*M* KCN with a current density of 4.6 amp/qdm, the yield was 75 percent with 10,000 alternations per minute, 55 percent with 20,000, and 40 percent with 300,000. With more dilute potassium cyanide less copper goes into solution. The amount of copper dissolving varies markedly with the previous treatment of the electrode. In a sodium bisulphate solution practically no copper dissolves with 14,000 alternations per minute. Zinc and nickel in potassium cyanide solution behave like copper; but silver is practically insoluble so soon as the alternations reach 4000 per minute.

W. D. B.

The principle of the application of electrical endosmose and of the allied phenomena of the colloidal state. *G. Bredig. Zeit. Elektrochemie*, 9, 738 (1903). — This is merely a review of the actual paper and gives only the merest outlines. *W. D. B.*

The technical application of endosmose. *v. Schwerin. Zeit. Elektrochemie*, 9, 739 (1903). — Peat is now dehydrated successfully by electrical endosmose, a cubic meter of water being removed for an expenditure of about 15 kilowatt hours. A great deal of moisture is left in the peat; but enough is removed and at such a cost to make peat available as a fuel. *W. D. B.*

Electrolytic copper refining. *W. D. Bancroft. Trans. Am. Electrochem. Soc.* 4, 55 (1903). — This is essentially an abstract of a paper by Schwab and Baum (7, 493). *W. D. B.*

On bipolar electrodes. *A. Brochet and C. L. Barillet. Zeit. Elektrochemie*, 9, 251 (1903). — The authors have studied the behavior of an interposed metallic diaphragm which does not divide the solution into two parts. When the diaphragm is polarizable, no current passes through it until the current density exceeds a definite minimum. With a so-called non-polarizable diaphragm, a portion of the current always passes through it, the percentage increasing with increasing current density. *W. D. B.*

On metal diaphragms. *A. Brochet. Zeit. Elektrochemie*, 9, 439 (1903). — A general discussion of the whole question of metal diaphragms. *W. D. B.*

On bipolar electrodes and metallic diaphragms. *H. Danneel. Zeit. Elektrochemie*, 9, 256 (1903). — Experiments were made with metallic wires or with carbon rods inserted in the solution between the electrodes. The author makes the assumption that a wire completely immersed in a solution will behave like the same wire with its ends the same distance apart but the middle projecting out of the solution. The depolarization effects around the wire have been overlooked in the second case. There is a discussion of the possible use of metallic diaphragms in electrolytic work and there are some remarks on the experiments of Brochet and Barillet (two reviews back). *W. D. B.*

The electrolysis of fused lead chloride. *A. Appelberg. Zeit. anorg. Chem.* 36, 36 (1903). — Using a V-tube or a cylindrical tube the yield of lead and of chlorine falls off with decreasing current density, reaching zero for a definite small current density. At the higher current densities the anode and cathode efficiencies are about the same; but the two differ for low current densities, probably owing to the different conditions under which the experiments were made. The addition of sodium or potassium chloride to the melt decreases the solubility of the lead and increases the yield. Addition of ferric chloride decreases the yield. The change of the yield with the current density is given fairly accurately by the formula of Lorenz. *W. D. B.*

On valve action and disintegration of copper anodes. *F. Fischer. Zeit. Elektrochemie*, 9, 50 (1903). — With a small copper wire anode (60 mm<sup>2</sup> surface), a large copper cathode, sulphuric acid of maximum conductivity and a potential difference of 20 volts, the copper anodes disintegrate, filling the solution with pulverulent copper. The author shows that this is due to the for-

mation of a surface film with a low conductivity. This heats until it is blown off by water vapor when cuprous sulphate is thrown into the solution, there decomposing into cupric sulphate and copper. The phenomenon disappears if the electrode is kept cooled. With a more dilute acid, cuprous hydroxide is formed.

W. D. B.

**Present status of the electrolytic dissociation theory.** *W. D. Bancroft. Trans. Am. Electrochem. Soc. 4, 175 (1903).* — A brief statement of some of the arguments for and against the electrolytic dissociation theory. Attention is drawn to the question whether there is anything abnormal about infinitely dilute aqueous salt solutions.

W. D. B.

**The thermochemistry of the theory of electrolytic dissociation.** *J. W. Richards. Trans. Am. Electrochem. Soc. 4, 137 (1903).* — "Whatever the ions are, they are not the chemical constituents from which the compound was formed, and the separation of a molecule into ions is not a destruction of the compounds or a resolution of it into its chemical constituents." As this is not disputed, it is hard to see any advance in the argument leading up to this conclusion. The author defines the heat of ionization of an element as the heat given out in changing it from a free molecular element into the state of a combined dissolved ion. Postulating the single potential difference for the mercury-sulphate electrode as  $-0.89$  volt and ignoring any possible temperature coefficient, the author calculates the heats of ionization for a number of basic and acid radicals.

Since the author looks upon a dilute solution of caustic soda as containing "combined Na" and "combined OH", the heat of neutralization cannot be the heat of formation of water from hydrogen and hydroxyl as ion. The author looks upon it as the heat evolved when gaseous water is condensed into liquid water. A special calculation shows that this heat effect might be 13700 calories for certain concentrations.

W. D. B.

**Theoretical properties of free ions in solutions.** *E. F. Roeder. Trans. Am. Electrochem. Soc. 4, 159 (1903).* — "The main result of the whole theory of free ions is, in my opinion, that it gives us a mechanical model which illustrates electrolytic phenomena in solutions, that it resolves the electrolytic phenomena into a mechanics of ions, that it is a simple scheme enabling us to prophesy what will happen in a given solution under given conditions." The author goes on to state clearly what properties we attribute to the free ions.

W. D. B.

**Abnormal electrolytes.** *P. Walden. Zeit. phys. Chem. 43, 385 (1903).* — Approximate measurements of the electrical conductivity of solutions of ninety-five typical substances (elements, inorganic or organic compounds) in liquid sulphur dioxide were made. Using the latter solvent accurate conductivity determination of solutions of the following substances were made: bromine, iodine chloride and trichloride, dimethyl ammonium chloride, phosphorus tribromide and pentabromide, arsenic tribromide, sulphur monobromide, antimony pentabromide, tin tetrachloride and tetrabromide, phosphorus oxy-bromide, sulphuryl chloride, quinoline, pyridine,  $\alpha$ -picoline, theine, dimethyl pyrone, triphenyl carbinol, trimethyl carbinol, triphenylmethyl, triphenylmethyl per-

oxide, triphenylmethyl acetoacetic ester, limonene, anthracene, phorone, triphenylmethyl chloride, the double salt of the latter with tin tetrachloride, triphenylmethyl bromide and iodide, tetramethyl ammonium chloride and bromide, trimethyl sulphonium iodide, trimethyl methyl iodide, dipentene dihydro-iodide,  $\alpha$ -bromisobutyryl bromide, mono-brom-acetyl bromide. In arsenic trichloride as solvent the conductivity of solutions of the following was ascertained: iodine, and the chloride, bromide, trichloride and pentabromide of iodine, phosphorus pentabromide, tin tetraiodide, quinoline, methylcyanide, dimethyl pyrone,  $\alpha$ -bromisobutyryl bromide. In sulphuryl chloride as solvent the conductivity of solutions of bromine, of iodine, and of iodine chloride, trichloride, and bromide was measured. In addition the conductivity of solutions of iodine in ether, acetic aldehyde and nitrogen tetroxide was determined; quinoline was also measured in phosphorus oxy-chloride, dimethyl pyrone, methyl cyanide, iodine chloride in phosphorus trichloride, and bromine, and iodine chloride and bromide in nitrogen tetroxide.

Measurable electrical conductivity was observed in most of the solutions mentioned. It is especially interesting that bromine when dissolved in liquid sulphur dioxide yields a solution with appreciable conductivity, as does also iodine in sulphuryl chloride. In explanation the author expresses the view that bromine and iodine molecules are salt-like in character, and that they are electrolytically dissociated in the solutions in question, which involves the assumption that these elements act as both cations and anions.

Adhering to the theory of electrolytic dissociation, the author holds that because of the electrical conductivity of the solutions investigated, the solutes in the latter must be electrically dissociated. A large amount of space is devoted to the consideration of the question into what ions the various substances dissociate. The conclusions reached as to what the various ions are are, however, merely assumptions. Appeals to authority are frequently made, the opinions of other writers being cited to strengthen the author's views. Some of the opinions are spoken of as authoritative. It is particularly unfortunate, however, that the author should (on p. 394) try to convey the impression that Lothar Meyer, when writing upon the subject of dissociation and its importance in causing chemical change, meant electrolytic dissociation, for it is well-known that the latter never favored the theory of electrolytic dissociation.

The many experimental facts contained in this article form a valuable contribution to our knowledge of electrolytic solutions. L. K.

**Note on some theoretical considerations in the construction of resistance furnaces.** *F. A. J. Fitzgerald. Trans. Am. Electrochem. Soc.* 4, 9 (1903).—A consideration of the factors affecting radiation and consequently the efficiency of graphite, the carborundum and the siloxicon furnace. W. D. B.

**Manufacture of iron and steel in the electric furnace.** *H. Goldschmidt. Zeit. Elektrochemie*, 9, 647 (1903).—An account of the Stassano, Héroult, Keller and Kjellin furnaces for making steel. A valuable bibliography is also appended. W. D. B.

**Advances in electro-metallurgy of iron production.** *M. Ruthenburg. Trans. Am. Electrochem. Soc.* 4, 19 (1903).—In the author's furnace a mag-

netic ore which has previously been magnetically concentrated, is brought into a magnetic zone and agglomerated. As soon as it ceases to be magnetic, it drops into the soaking pit and is there reduced by hot carbon monoxide or hot hydrocarbons. The power necessary to agglomerate one ton of ore is 250 kilowatt hours.

W. D. B.

#### *Dielectricity and Optics*

**On the variation of the dielectric constant of a fluid with temperature.** *K. Tangl. Drude's Ann.* 10, 748 (1903). — Drude's method was used for measuring the constant for benzene, toluene, xylene, carbon disulphide, chloroform and ether. The temperature interval was between 20° and 200°. For ether the measurements were made over the critical temperature. An empirical formula is given which represents very well all except ether. This shows a rapid fall near the critical temperature. The Clausius-Mossotti formula gives a constant value only for xylene.

H. T. B.

**Determination of the dielectric constant of crystals with electric waves.** *W. Schmidt. Drude's Ann.* 11, 114 (1903). — The method which was used by the author and previously described (7, 492) was not applicable for constants over 81. In order to overcome this difficulty, where the constant exceeded this value in one direction in a crystal, the dielectric constant of the powdered crystals was determined, and a mean value obtained in this way. With the measurements in the two other directions and this mean value, the higher value can be calculated. The constant of a number of the elements is measured and it is shown that crystallized sulphur and carbon follow Maxwell's rule. In conclusion, the dielectric constant is studied in relation to chemical composition.

H. T. B.

**On the laws governing electric discharges in gases at low pressures.** *W. R. Carr. Phil. Trans.* 201A, 403 (1903). — "The law governing electric discharges between parallel plates in a uniform field, in any gas, for pressures at and below the critical pressures, is that which Paschen found to hold with spherical electrodes for high pressures, viz., that, with a given spark potential, the pressure at which discharge occurs is inversely proportional to the distance between the electrodes.

"The value of the spark potentials are not influenced at any pressures by the size of the electrodes, provided the discharge takes place in a uniform field.

"Plates of iron, zinc, aluminum, and brass were in turn used as electrodes, but the material out of which the electrodes were made was not found to affect the value of the spark potentials at any pressure.

"When the discharge was compelled to pass in a uniform field between parallel plates the minimum spark potential in any gas was found to be a physical constant for that gas, being independent of the pressure and of the distance between the electrodes.

"Evidence has been adduced which indicates that Paschen's law is applicable to discharges in a uniform field between parallel plates as long as the distance between the electrodes is greater than the diameter of the sphere of molecular action.

"The minimum spark potential has been shown to vary with different

gases. The results obtained with a large number of elementary and compound gases show that the minimum spark potential is a property of the atom rather than the molecule, and that for any selected gas it may be calculated by the application of a simple additive law. *W. D. B.*

The electrical conductivity imparted to a vacuum by hot conductors. *O. W. Richardson. Phil. Trans.* 201A, 497 (1903). — The author assumes that raising the temperature of a metal increases the average velocity of the corpuscles without increasing the energy required to take an ion through the surface. A formula for the change of the saturation current with the temperature can then be deduced, involving two new constants, of the number of ions in unit volume of the metal and of the work done by an ion in passing through the surface. According to this formula the saturation current is an exponential function of the temperature. Experimentally it was found that this current changed from  $10^{-10}$  to  $10^{-3}$  amp/cm<sup>2</sup> when platinum passed from 1000° to 1600°; from  $10^{-11}$  to  $2 \times 10^{-2}$  amp/cm<sup>2</sup> when sodium was heated from 100° to 450°; and from  $10^{-8}$  to 2 amp/cm<sup>2</sup> when carbon is heated from 1200° to the temperature at which the filament broke. The theory calls for a current when the hot metal is charged positively which shall be vanishingly small in comparison with that which flows when the metal is charged negatively. This is actually the case. In a postscript the author admits the possibility of his results being seriously affected by occluded gases. *W. D. B.*

On the supposed electrolysis of water-vapor. *F. A. Lidbury. Trans. Am. Electrochemical Soc.* 4, 127 (1903). — The author finds that "in the partial decomposition of water vapor by the electric discharge the hydrogen and oxygen liberated tend to separate and to take up different positions in the tube, the hydrogen collecting at both anode and cathode and the oxygen in the middle of the tube." *W. D. B.*

The preparation of argon by means of electric sparks. *A. Becker. Zeit. Elektrochemie*, 9, 600 (1903). — The author describes an improved apparatus for isolating argon by sparking the nitrogen with oxygen in presence of an alkaline solution. *W. D. B.*

Excited radioactivity and the method of its transmission. *E. Rutherford. Phil. Mag.* [6], 5, 95 (1903). — The author uses the word excited in place of induced when speaking of the radioactivity deposited on a negatively charged body exposed to the air or to the emanation from thorium or radium. The cause of the radioactivity being, as it is shown in the present paper, the deposit of radioactive matter, transmitted by positively charged carriers, the word induced, which expresses action at a distance, is not so suitable. The positively charged bodies forming the carriers are due to the expulsion of a negatively charged body from the molecules of the emanation. Further properties are cited and reference is made to the evidence of continuous chemical change in radioactive matter. *H. T. B.*

The magnetic and electric deviation of the easily absorbed rays from radium. *E. Rutherford. Phil. Mag.* [6], 5, 177 (1903). — In this paper the author gives direct experimental proof of the deviability of the  $\alpha$ -rays from radium, and

shows by the direction of the deviation that they consist of positively charged bodies projected with a great velocity.

The difficulty of the measurements will be understood when it is seen that the rays projected at right angles to a magnetic field strength of 10000 C. G. S. units describe the arc of a circle of radius 39 cms, where the cathode rays under similar conditions would be bent into a circle of radius about 0.01 cm.

The value deduced for the velocity of the rays is  $2.5 \times 10^9$  cm per second, and the ratio of charge to mass,  $\frac{e}{m}$ , was found to be  $6 \times 10^3$ . This latter value however, gives only the order of the ratio owing to the difficulty of measuring the electrostatic deviation accurately. In conclusion some general considerations are given which show the relation of the present results to the author's previous work.

H. T. B.

**The radioactivity of uranium.** *E. Rutherford and F. Soddy. Phil. Mag.* [6] 5, 441 (1903). — The authors study uranium in the light of the theory put forward by them for thorium. Experiments extending over 160 days were carried out to determine the rate of loss of the activity of separated UrX, and the rate of recovery of the activity of uranium freed from UrX. Since the  $\alpha$ -rays were inseparable with the uranium and the  $\beta$ -rays were removed by the UrX, the problem resolved itself into a measurement of the rate of recovery and decay of the  $\beta$  or penetrating rays.

H. T. B.

**The radioactivity of radium and thorium.** *E. Rutherford and F. Soddy. Phil. Mag.* [6] 5, 445 (1903). — Measurements of the rate of decay of the radium emanation show that it falls to half value in four days, while the thorium emanation falls to the same value in one minute. For both thorium and radium, solution in water as well as heat, increases their emanating power. On the assumption of the occlusion of the emanation in the radium the ratio of the amount given off in the first rush as solution to the amount given off in any subsequent period is calculated. The amount of emanation stored up in a non-emanating radium compound was calculated to be nearly 500,000 times the amount produced per second. This was also verified in a very complete way by experiment. Exactly the same considerations apply to thorium except that the very rapid rate of decay of the emanation makes the effect less marked. The converse of the changes that occur when a solid radium preparation is dissolved in water and the emanation liberated was next studied. Radium chloride was dissolved in water and a current of air sent through the solution. The radioactivity of the salt, obtained by quickly evaporating the solution, was found to have been reduced to a minimum, but the recovery of the activity was observed over a period of three weeks.

The recovered activity remained constant at about four times the original value. The recovery curve and the decay curve of the emanation were found to exactly correspond. The radiations from radium consist like thorium and uranium of  $\alpha$  and  $\beta$ -rays. The non-separable activity of radium consists of  $\alpha$ -rays. A third type of radiation which is exceedingly penetrating is also emitted. The rays are in all cases the first to be produced, the  $\beta$ -rays only resulting in the last stages of the process of disintegration.

H. T. B.

**The condensation of the radioactive emanations.** *E. Rutherford and F. Soddy. Phil. Mag.* [6] 5, 561 (1903). — It is shown that the emanations from radium and thorium are condensed in a tube immersed in liquid air. An elaborate series of experiments was undertaken to determine the exact temperature of condensation and thereby to show more conclusively the material nature of the emanations. Temperatures were measured by a copper spiral with potential terminals and a Weston millivoltmeter, and very satisfactory results were obtained at these low temperatures. It was found that the thorium emanation begins to condense at  $-120^{\circ}\text{C}$ , although the point is not sharply defined as in the case of radium which condenses and volatilizes between  $-153^{\circ}$  and  $-150^{\circ}\text{C}$ .

H. T. B.

**On radioactive change.** *E. Rutherford and F. Soddy. Phil. Mag.* [6] 5, 576 (1903). — The authors start out by giving the evidence of the material nature of the products of radioactive change such as the removal of ThX and UrX, the condensation of the radioactive emanations, and the volatilization of the excited radioactivity. It is pointed out that the products differ from ordinary matter only in their quantity, which is far below the limit reached by ordinary methods of chemical and spectroscopic analysis. Radioactivity being an accompaniment of chemical change it is only by the phenomenon of radioactivity that this matter makes itself known. For this reason the ultimate product of the changes, which cannot be radioactive, cannot be known since it will be beyond the range of methods of experiments. A non-separable activity must always exist in the radioactive elements, representing the first change of the radio-element into the first new products that is produced.

The material nature of the radiations themselves is next discussed. The  $\alpha$ -rays, which are non-separable, have been shown to be particles of the order of the hydrogen atom projected with a great velocity, and in all cases they represent over 99 per cent of the total energy radiated. The  $\beta$ -rays only appear after the processes of change near completion, and like cathode rays consist of particles  $1/1000$ th of the hydrogen atom. It is shown that there is every reason to suppose that the expulsion of a charged particle not merely accompanies the change but that it actually is the change.

The law of radioactive change is deduced and states that the proportional amount of radioactive matter that changes in unit time is a constant. The rate of change of the system at any time is always proportional to the amount remaining unchanged.

The idea of the conservation of radioactivity is introduced "since radioactivity must be regarded as a process which lies wholly outside the sphere of known controllable forces and cannot be created, altered or destroyed." Being proportional only to the quantity of matter involved it is like gravitation, although differing from this latter in not being a universal property of matter. The authors take up the question of the relation of polonium to the other radioactive elements, the permanence of the radioactivity being essential before any substance can be classed as a radio-element. All elements heavier than uranium, which exist, are probably radioactive, but are present in exceedingly minute quantities.

The relation of radioactive change to chemical change is discussed, and it



is shown that the former is entirely atomic. The word Metabolon is suggested for the fragments of atoms or new atoms which are formed during the various stages of disintegration, and which exist only for a short space of time in the general evolution.

In estimating the internal energy of the chemical atom it is calculated that 10 gram calories is the least possible energy liberated by the radioactive change of 1 gram of pure radium. This shows that the energy of atomic change is at least twenty thousand and possibly a million times as great as the energy of molecular change such as the union of hydrogen and oxygen.

In conclusion the authors give estimates of the energy of the rays, and make some important suggestions in regard to the stability of the chemical elements and the general relation to cosmical physics. H. T. B.

**On the rays from radioactive lead.** *A. Korn and E. Strauss. Drude's Ann.* 11, 397 (1903). — It is shown that two actions may be observed in the radioactive lead preparation studied by Hofmann. The explanation of the first, which is given by the authors, is a solution of the substance in the surrounding air, causing a strong electrical discharging action. This action is shown to have no penetrating power, and is not deflected by a strong magnetic field.

The explanation offered for the second is that rays are produced which cause the greater part of the photographic action. These rays are very penetrating, are deflected by a magnetic field and are strengthened by cathode rays. The first action is unaffected by cathode rays. It is shown that the two actions may be separately influenced by chemical treatment. In conclusion, two methods are described for preparing the lead salt. H. T. B.

**On the existence of a relationship between the spectra of some elements, and the squares of their atomic weights.** *W. M. Watts. Phil. Mag.* [6] 5, 203 (1903). — In general an increase in atomic weight produces a shift towards the red end of the spectrum. From the examples cited it appears that the amount of the shift in many cases admits of simple expression in terms of the squares of the atomic weights. H. T. B.

**The position of radium in the periodic system according to its spectrum.** *C. Runge and J. Precht. Phil. Mag.* [6] 5, 476 (1903). — It is found that the strongest lines of radium are exactly analogous to the strongest lines of barium and the corresponding lines of the related elements Mg, Ca and Sr, and that it must be classed along with these elements in a group of chemically allied elements. The atomic weight as deduced by the authors is 258, which is somewhat higher than the value found by Mme. Curie, *i. e.*, 225. The higher value is probably more nearly correct, as the authors suggest, in the light of recent work. H. T. B.

**On the Bunsen flame spectrum of radium.** *C. Runge and J. Precht. Drude's Ann.* 10, 655 (1903). — A more careful study is made of the spectrum of radium than was made by Giesel. The salt used was radium bromide. A table of the spectrum is given in the paper. The strongest characteristic line is a sharp blue line at 4826. H. T. B.

**The spectra of hydrogen and the reversed lines in the spectra of gases.** *J. Trowbridge. Phil. Mag.* [6] 5, 153 (1903). — Experiments described in a

previous paper (7, 552) are continued with quartz tubes. These tubes were 8 cm in length with a capillary 4 cm long and 2 mm in diameter.

The result of the investigation with powerful condenser discharge shows that a reversal may result from an action on the photographic plate that is used. With the quartz tubes a gas, which otherwise showed a continuous spectrum, showed a large region in the ultra-violet traversed by both dark and bright lines and bands.

H. T. B.

On the dependence of the refractive index of gases on temperature. *G. W. Walker. Phil. Trans.* 201A, 435 (1903). — The author used Jamin's interference method to determine the refractive indices of air, hydrogen, carbon dioxide, ammonia, and sulphur dioxide. The measurements refer to sodium light and are believed to be accurate at least to one part in five hundred. The temperature coefficient for the refractive index of these gases was found to be: air, 0.00360; hydrogen, 0.00350; carbon dioxide, 0.00380; ammonia, 0.00390; sulphur dioxide, 0.00416. The temperature coefficients have a probable error of about  $\pm 1$  percent. These values are all lower than those of Mascart and are nearer to the coefficients of expansion though not identical with them.

W. D. B.

The dependence of the refractive index of salt solutions on the concentration. *J. Wallot. Drude's Ann.* 11, 593 (1903). — The different interpolation formulas are studied, and an attempt made to ascribe a physical meaning to various constants. An attempt is also made to find the formula that comes nearest in theoretical import to the rule of mixtures, which gives the relation between refractive index, density and concentration.

H. T. B.

On the action of inorganic compounds on the rotation of quinic acid. *E. Rimbach and P. Schneider. Zeit. phys. Chem.* 44, 467 (1903). — The authors have studied the effect, on quinic acid, of solutions of molybdenum, tungsten, uranium, titanium, zirconium, cerium, thorium, tin, boron and arsenic compounds. In all cases there is an increase of rotation which often passes through a maximum for a molecular ratio of one to one. Some experiments were also made with zirconium salts in solutions of malic and tartaric acids.

W. D. B.

The problem of optical activity with asymmetric nitrogen. *E. Wedekind. Zeit. phys. Chem.* 45, 235 (1903). — The author has prepared some optically active nitrogen compounds. They differ from the carbon compounds in that they cannot be prepared by means of bacteria and that they change back readily into the optically neutral state. The optically active nitrogen compounds are ammonium salts and furnish optically active cations in aqueous solution.

W. D. B.

On chemical dynamics and statics under the influence of light. *M. Wildermann. Phil. Trans.* 199A, 337 (1902). — Reviewed (6, 439) from *Zeit. phys. Chem.* 41, 87 (1902).

On the action of canal rays on zinc oxide. *T. Tafel. Drude's Ann.* 11, 613 (1903). — The phenomenon, which was first observed by Wien for the oxides of Mg, Al and Zn, that when freshly prepared they fluoresce for a short time

under the influence of canal rays is the basis of the author's study of zinc oxide. It is shown that fresh white oxide gives a green fluorescence, which rapidly fades to a brown, and finally, after a long exposure to the rays and shaking, to a coffee brown throughout the mass. No change in weight is associated with the process. The same brown color can be produced by highly compressing the fresh oxide. This compressed oxide does not show the preliminary green fluorescence under the influence of the rays. The conclusion is reached that the canal rays produce the same molecular change as the high pressure. Three kinds of oxide are described, two white and one brown. The difference in the white oxides is one of preparation. The oxide produced by browning metallic zinc shows the preliminary green fluorescence, while that produced chemically from acid zinc sulphate and sodium carbonate does not. Cathode rays are shown to produce a much less marked effect.

H. T. B.

The action of pressure on phosphorescent sulphides. *P. Waentig. Zeit. phys. Chem.* 44, 499 (1903).—When certain phosphorescent sulphides are ground to powder in a porcelain or agate mortar, they lose their phosphorescent power to a great extent and the color changes to a complementary one. The author intends to study this phenomenon in detail.

W. D. B.

An optical pyrometer. *L. Holborn and F. Kurlbaum. Drude's Ann.* 10, 225 (1903).—A platinum iridium filament is placed in the path of the ray from a glowing body, the temperature of which it is desired to measure. A lens projects the image of the filament and the rays from the body through a red-glass window. When, by means of an electric current, the filament is heated to the same temperature it can no longer be seen. The filament is standardized by means of a black body and thermocouple, and a curve constructed giving the relation between temperature and current strength. The apparatus is very simple, and a good description is given of the experiments carried out with it including much of value and interest.

H. T. B.

#### *Crystallography, Capillarity and Viscosity*

Effects of strain on the crystalline structure of lead. *J. C. W. Humfrey. Phil. Trans.* 200A, 225 (1903).—Experiments were made with single crystals of a very pure lead. When such a crystal is strained in tension, it elongates, due to the numerous small slips along the gliding planes of the crystal. The slip along the gliding planes does not take place to an equal extent right across the specimen.

The recrystallization, observed after the strain, is shown to be an effect subsequent in time. By heating to 60° after straining, the rate of recrystallization can be accelerated.

W. D. B.

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==THE==  
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## NOTE ON THERMODYNAMIC SURFACES

BY J. E. TREVOR

### Conditions of stability

In his investigation of the energy surface for a one-component system,<sup>1</sup> Gibbs has given an ingenious and convincing demonstration of the theorem that, when  $p, \theta$  are the pressure and absolute temperature of a thermodynamic system in a state of dissipated energy determined by the volume  $v$  and the entropy  $\eta$ , and  $v + \delta v, \eta + \delta \eta$  is another state, not a state of dissipated energy at  $p, \theta$ , it is true that

$$\delta e + p\delta v - \theta\delta\eta > 0.$$

Otherwise stated, in all variations of state imagined as occurring from a state of stable equilibrium at  $p, \theta$  to a state not in stable equilibrium at  $p, \theta$ ,

$$\delta e > -p\delta v + \theta\delta\eta.$$

It is possible, however, to have a succession of univariant states or of invariant states that are all states of stable equilibrium at  $p, \theta$ . In such a case, no one state of the succession will spontaneously pass into another, the equilibrium of each state will be 'neutral'. If the change through the succession of stable states be reversibly effected, Gibbs's demonstration yields

$$\delta e = -p\delta v + \theta\delta\eta.$$

For a state to be one of stable equilibrium at the pressure and temperature  $p, \theta$ , it is therefore necessary that, in all variations of the state,

$$\delta e \geq -p\delta v + \theta\delta\eta.$$

On passing from any point  $v, \eta$  on the energy surface

$$e = e(v, \eta)$$

for one-phase states, or for states of two given phases, or of three given phases, to an adjacent point  $v + \delta v, \eta + \delta \eta$  on the surface,

<sup>1</sup> Trans. Conn. Acad. 2, 382 (1873).

$$\delta e = \frac{\partial e}{\partial v} \delta v + \frac{\partial e}{\partial \eta} \delta \eta + \frac{1}{2} \left( \frac{\partial^2 e}{\partial v^2} (\delta v)^2 + 2 \frac{\partial^2 e}{\partial v \partial \eta} \delta v \delta \eta + \frac{\partial^2 e}{\partial \eta^2} (\delta \eta)^2 \right) + \dots;$$

whence, because of the above criterion of stability, which may be written

$$\delta e \geq \frac{\partial e}{\partial v} \delta v + \frac{\partial e}{\partial \eta} \delta \eta,$$

it appears that the condition that the point  $v, \eta$ , shall represent a state of equilibrium is

$$\frac{\partial^2 e}{\partial v^2} (\delta v)^2 + 2 \frac{\partial^2 e}{\partial v \partial \eta} \delta v \delta \eta + \frac{\partial^2 e}{\partial \eta^2} (\delta \eta)^2 \geq 0$$

for all values of  $v, \eta$ . This condition expresses that no portion of the surface may lie below the tangent plane passing through the point  $v, \eta$ . It expresses, in particular, that a succession of states in neutral equilibrium is represented by the points on a line common to the surface and the plane tangent thereto at the point  $v, \eta$ ; and that, at a point representing a state of stable equilibrium that is not also a state of neutral equilibrium, the surface is convex downward in all directions. All portions of the surface that do not satisfy these conditions must represent thermodynamically instable states.

When

$$e = e(v, \eta)$$

is the equation of the continuous succession of stable and instable one-phase states, a point representing a state of stable equilibrium must satisfy the condition

$$\frac{\partial^2 e}{\partial v^2} (\delta v)^2 + 2 \frac{\partial^2 e}{\partial v \partial \eta} \delta v \delta \eta + \frac{\partial^2 e}{\partial \eta^2} (\delta \eta)^2 > 0.$$

The necessary and sufficient conditions for this quadratic expression to be positive, i. e., for the surface to be convex downward in every direction at  $v, \eta$ , are

$$H(e) > 0, \quad \partial^2 e / \partial v^2 > 0,$$

where  $H(e)$  denotes the hessian of the function  $e(v, \eta)$ . A con-

sequence of these 'conditions of stability' is the further inequality

$$\frac{\partial^2 e}{\partial \eta^2} > 0.$$

#### A problem

It was further pointed out by Gibbs that the thermodynamic properties represented by the surface

$$e = e(v, \eta)$$

are represented by the surfaces

$$f = f(v, \theta)$$

$$g = g(p, \eta)$$

$$h = h(p, \theta);$$

the functions  $f, g, h$  being defined by the equations

$$f(v, \theta) = e - \theta \eta$$

$$g(p, \eta) = e + p v$$

$$h(p, \theta) = e + p v - \theta \eta;$$

wherefore we have the set of differential equations

$$de = -p dv + \theta d\eta$$

$$df = -p dv - \eta d\theta$$

$$dg = v dp + \theta d\eta$$

$$dh = v dp - \eta d\theta.$$

We may now seek to determine the curvatures of those portions of the  $f, g, h$  surfaces that represent one-phase stable states, i. e., that correspond to the convex portions of the primitive energy surface.

#### Auxiliary equations

In this search we shall require to use a series of equations, which shall now be assembled for reference. We have

$$-dp = \frac{\partial^2 e}{\partial v^2} dv + \frac{\partial^2 e}{\partial v \partial \eta} d\eta$$

$$d\theta = \frac{\partial^2 e}{\partial v \partial \eta} dv + \frac{\partial^2 e}{\partial \eta^2} d\eta;$$

whence, by successive elimination of  $d\eta$  and  $dv$ ,

$$H(e) \cdot dv = \begin{vmatrix} -dp & \frac{\partial^2 e}{\partial v \partial \eta} \\ d\theta & \frac{\partial^2 e}{\partial \eta^2} \end{vmatrix}, \quad H(e) \cdot d\eta = \begin{vmatrix} \frac{\partial^2 e}{\partial v^2} & -dp \\ \frac{\partial^2 e}{\partial v \partial \eta} & d\theta \end{vmatrix};$$

whence follow the desired equations,

$$(a) \quad \left( \frac{\partial v}{\partial p} \right)_\theta = -\frac{1}{H(e)} \frac{\partial^2 e}{\partial \eta^2} \quad \left| \quad \left( \frac{\partial \eta}{\partial \theta} \right)_p = \frac{1}{H(e)} \frac{\partial^2 e}{\partial v^2} \quad (c)$$

$$(b) \quad \left( \frac{\partial v}{\partial \theta} \right)_p = -\frac{1}{H(e)} \frac{\partial^2 e}{\partial v \partial \eta} \quad \left| \quad \left( \frac{\partial \eta}{\partial p} \right)_\theta = -\frac{1}{H(e)} \frac{\partial^2 e}{\partial v \partial \eta} \quad (d)$$

and from these, by division,

$$(e) \quad \left( \frac{\partial v}{\partial \eta} \right)_\theta = -\frac{\partial^2 e}{\partial \eta^2} : \frac{\partial^2 e}{\partial v \partial \eta} \quad \left| \quad \left( \frac{\partial \eta}{\partial v} \right)_p = -\frac{\partial^2 e}{\partial v^2} : \frac{\partial^2 e}{\partial v \partial \eta} \quad (f)$$

#### The second derivatives

We now require to determine the signs of the second derivatives, and of the hessian, of each of the functions  $f, g, h$  at points representing stable one-phase states.

For  $\partial^2 f / \partial v^2$ , we have

$$\begin{aligned} \frac{\partial f}{\partial v} &= -p \\ \frac{\partial^2 f}{\partial v^2} &= -\left( \frac{\partial p}{\partial v} \right)_\theta \\ &= H(e) : \frac{\partial^2 e}{\partial \eta^2} \\ &> 0, \end{aligned}$$

by equation (a).

For  $\partial^2 f / \partial \theta^2$ , we have

$$\begin{aligned} \frac{\partial f}{\partial \theta} &= -\eta \\ \frac{\partial^2 f}{\partial \theta^2} &= -\left( \frac{\partial \eta}{\partial \theta} \right)_v \\ &= -1 : \left( \frac{\partial \theta}{\partial \eta} \right)_v \\ &= -1 : \frac{\partial^2 e}{\partial \eta^2} \\ &< 0. \end{aligned}$$

For  $H(f)$ , we have

$$\begin{aligned}\frac{\partial^2 f}{\partial v \partial \theta} &= - \left( \frac{\partial p}{\partial \theta} \right)_v \\ &= - \left( \frac{\partial p}{\partial \eta} \right)_v : \left( \frac{\partial \theta}{\partial \eta} \right)_v \\ &= \frac{\partial^2 e}{\partial v \partial \eta} : \frac{\partial^2 e}{\partial \eta^2}.\end{aligned}$$

Hence we find

$$\begin{aligned}H(f) &= \frac{\partial^2 f}{\partial v^2} \frac{\partial^2 f}{\partial \theta^2} - \left( \frac{\partial^2 f}{\partial v \partial \theta} \right)^2 \\ &= \frac{\frac{\partial^2 e}{\partial v^2} \frac{\partial^2 e}{\partial \eta^2} - \left( \frac{\partial^2 e}{\partial v \partial \eta} \right)^2}{\frac{\partial^2 e}{\partial \eta^2}} \cdot \frac{-1}{\frac{\partial^2 e}{\partial \eta^2}} - \frac{\left( \frac{\partial^2 e}{\partial v \partial \eta} \right)^2}{\left( \frac{\partial^2 e}{\partial \eta^2} \right)^2} \\ &= - \frac{\partial^2 e}{\partial v^2} : \frac{\partial^2 e}{\partial \eta^2} \\ &< 0.\end{aligned}$$

For  $\partial^2 g / \partial p^2$ , we have

$$\begin{aligned}\frac{\partial g}{\partial p} &= v \\ \frac{\partial^2 g}{\partial p^2} &= \left( \frac{\partial v}{\partial p} \right)_\eta \\ &= 1 : \left( \frac{\partial p}{\partial v} \right)_\eta \\ &= -1 : \frac{\partial^2 e}{\partial v^2} \\ &< 0.\end{aligned}$$

For  $\partial^2 g / \partial \eta^2$ , we have

$$\begin{aligned}\frac{\partial g}{\partial \eta} &= \theta \\ \frac{\partial^2 g}{\partial \eta^2} &= \left( \frac{\partial \theta}{\partial \eta} \right)_p \\ &= (H)e : \frac{\partial^2 e}{\partial v^2} \\ &> 0,\end{aligned}$$

by equation (c).

For  $H(g)$ , we have

$$\begin{aligned}\frac{\partial^2 g}{\partial \rho \partial \eta} &= \left( \frac{\partial v}{\partial \eta} \right)_\rho \\ &= -\frac{\partial^2 e}{\partial v \partial \eta} : \frac{\partial^2 e}{\partial v^2},\end{aligned}$$

by equation (f). Hence we have

$$\begin{aligned}H(g) &= \frac{\partial^2 g}{\partial \rho^2} \frac{\partial^2 g}{\partial \eta^2} - \left( \frac{\partial^2 g}{\partial \rho \partial \eta} \right)^2 \\ &= \frac{-1}{\frac{\partial^2 e}{\partial v^2}} \cdot \frac{\frac{\partial^2 e}{\partial v^2} \frac{\partial^2 e}{\partial \eta^2} - \left( \frac{\partial^2 e}{\partial v \partial \eta} \right)^2}{\frac{\partial^2 e}{\partial v^2}} - \frac{\left( \frac{\partial^2 e}{\partial v \partial \eta} \right)^2}{\left( \frac{\partial^2 e}{\partial v^2} \right)^2} \\ &= -\frac{\partial^2 e}{\partial \eta^2} : \frac{\partial^2 e}{\partial v^2} \\ &< 0.\end{aligned}$$

For  $\partial^2 h / \partial \rho^2$ , we have

$$\begin{aligned}\frac{\partial h}{\partial \rho} &= v \\ \frac{\partial^2 h}{\partial \rho^2} &= \left( \frac{\partial v}{\partial \rho} \right)_\rho \\ &= \frac{-1}{H(e)} \frac{\partial^2 e}{\partial \eta^2} \\ &< 0,\end{aligned}$$

by equation (a).

For  $\partial^2 h / \partial \theta^2$ , we have

$$\begin{aligned}\frac{\partial h}{\partial \theta} &= -\eta \\ \frac{\partial^2 h}{\partial \theta^2} &= -\left( \frac{\partial \eta}{\partial \theta} \right)_\rho \\ &= \frac{-1}{H(e)} \frac{\partial^2 e}{\partial v^2} \\ &< 0,\end{aligned}$$

by equation (c).

For  $H(h)$ , we have

$$\begin{aligned}\frac{\partial^2 h}{\partial \rho \partial \theta} &= \left( \frac{\partial v}{\partial \theta} \right)_\rho \\ &= \frac{-1}{H(e)} \frac{\partial^2 e}{\partial v \partial \eta},\end{aligned}$$

by equation (b). Hence we find

$$\begin{aligned}H(h) &= \frac{\partial^2 h}{\partial \rho^2} \frac{\partial^2 h}{\partial \theta^2} - \left( \frac{\partial^2 h}{\partial \rho \partial \theta} \right)^2 \\ &= \frac{-\frac{\partial^2 e}{\partial \eta^2}}{H(e)} \cdot \frac{-\frac{\partial^2 e}{\partial v^2}}{H(e)} - \left( \frac{\frac{\partial^2 e}{\partial v \partial \eta}}{H^2(e)} \right)^2 \\ &= 1 : H(e) \\ &> 0.\end{aligned}$$

These results are assembled in the following table :

$H(e) > 0$	$\frac{\partial^2 e}{\partial v^2} > 0$	$\frac{\partial^2 e}{\partial \eta^2} > 0$
$H(f) < 0$	$\frac{\partial^2 f}{\partial v^2} > 0$	$\frac{\partial^2 f}{\partial \theta^2} < 0$
$H(g) < 0$	$\frac{\partial^2 g}{\partial \rho^2} < 0$	$\frac{\partial^2 g}{\partial \eta^2} > 0$
$H(h) > 0$	$\frac{\partial^2 h}{\partial \rho^2} < 0$	$\frac{\partial^2 h}{\partial \theta^2} < 0$

### The curvatures

From these data it appears that the portions of the  $e, f, g, h$ -surfaces that represent stable one-phase states are convex in the case of the  $e$ -surface, concave in the case of the  $h$ -surface, and saddle-shaped in the other two cases. In particular, the  $f$ -surface is convex at  $v, \theta$  in the section parallel to  $v$ , and concave in the section parallel to  $\theta$ ; and the  $g$ -surface is convex at  $\rho, \eta$  in the section parallel to  $\eta$ , and concave in the section parallel to  $\rho$ .

It may be added that, whenever the primitive  $e$ -surface becomes concave at  $v, \eta$ , every curvature stated above will be changed into its opposite; and that, whenever the  $e$ -surface be-



comes convex in one coordinate section and concave in the other, the  $h$ -surface will be so also, while the  $f$ -surface and the  $g$ -surface will become dome-shaped. For when the hessian of a surface  $z = z(x, y)$  is positive the surface is dome-shaped, and is convex or concave according as

$$\frac{\partial^2 z}{\partial x^2} \quad \text{and} \quad \frac{\partial^2 z}{\partial y^2}$$

are both positive or both negative. When the hessian is positive these derivatives must have the same sign.

### Reciprocal character of the surfaces

It may be noted in the above that the Hessians of the  $e$  and  $h$  surfaces, and of the  $f$  and  $g$  surfaces, are the reciprocals of each other; that

$$H(e) \cdot H(h) = 1$$

$$H(f) \cdot H(g) = 1.$$

This is one aspect of the reciprocal relation between the  $e$  and  $h$  and the  $f$  and  $g$  surfaces, which appears most clearly when it is noted that the ordinate of a point in either surface of either pair appears in the other surface as the segment

$$z - \frac{\partial z}{\partial x} x - \frac{\partial z}{\partial y} y,$$

intercepted on the vertical axis by the tangent plane at the point; and that the horizontal coordinates of the one surface are the slopes of the other<sup>1</sup> (the changes of sign being due to taking  $+p$  instead of  $-p$  as a coordinate in two cases). This is exhibited in the tabulation:

Ordinate	Intercept	Coordinates	Slopes
$e$	$h$	$v, \eta$	$-p, \theta$
$h$	$e$	$p, \theta$	$v, -\eta$
$f$	$g$	$v, \theta$	$-p, -\eta$
$g$	$f$	$p, \eta$	$v, \theta$

<sup>1</sup> With respect to the  $e$  and  $h$  surfaces, this has been pointed out by Gibbs.

This reciprocity appears again in the relation

$$e + h = f + g,$$

which follows from the definition equations

$$e = e$$

$$h = e + pv - \theta\eta.$$

$$f = e - \theta\eta$$

$$g = e + pv.$$

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## THERMOMETRIC ANALYSIS OF SOLID PHASES

BY E. S. SHEPHERD

In a paper entitled "Synthetic Analysis of Solid Phases" Bancroft<sup>1</sup> has shown how the composition of the solid phase might be determined by temperature measurements, thus avoiding quantitative analysis either of the solution or the solid phase. It was pointed out that this method was especially desirable for the study of alloys, other systems in which it is impossible to free the solid phase from the mother liquor, in order to determine the composition analytically. While reviewing some measurements made by<sup>1</sup> Heycock and Neville<sup>2</sup> on the "Freezing-Points of Alloys of Gold, Cadmium, and Tin", it occurred to us to recalculate their data and see if we could not deduce from them the composition of the solid phases present.

The first point to be noticed and one which must be fixed firmly in mind in order to understand what follows, is, that the curves given by Heycock and Neville (Figs. 1, 2, and 3) are not freezing-point curves as we now define them. Only along the branch of the curve AB did they determine the freezing-point of the alloy. Along AB tin begins to separate and is the only solid phase. Beyond B, there is always a solid phase present from which we know that the temperature given on the curve cannot be that of the freezing-point and must be that of the boundary curve, along which we have already one solid phase and where tin is just beginning to separate from the solution. The real freezing-point curve or liquidus must rise rather abruptly since it does not appear in any of their measurements.

If now we remember that we are dealing with a system in which there is always one solid phase and that we are measur-

<sup>1</sup> Jour. Phys. Chem. 6, 178 (1902). This method is a natural corollary from principles first pointed out by Schreinemakers. Zeit. phys. Chem. 11, 81 (1893).

<sup>2</sup> Jour. Chem. Soc. 59, 936 (1891).

ing the temperature at which a second (tin) begins to appear, we shall be able to understand more readily the curves of Figs. 1, 2, and 3. The Roman numerals refer to the series of measure-

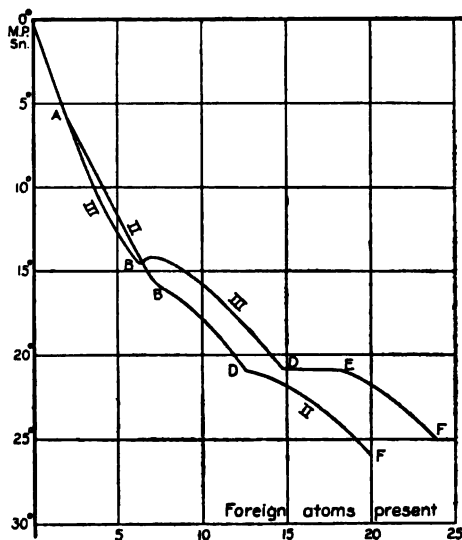


Fig. 1

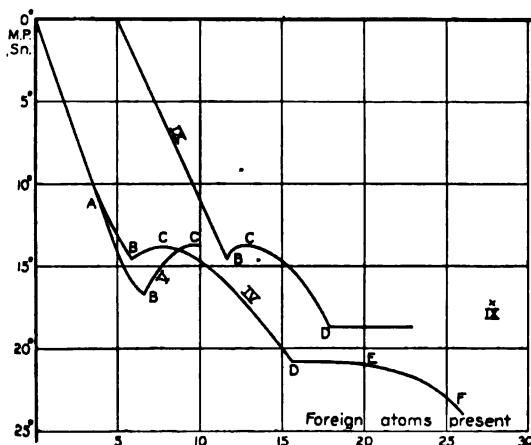


Fig. 2

ments from which the curves were obtained. The ordinates are degrees centigrade and measured *down* from the freezing-point

of tin. The abscissæ are the number of atoms of other metals present per one hundred atoms of tin. Along the branch OAB either gold or cadmium has been added, and both in curves II and III. On cooling, the tin begins to separate at lower and lower temperatures until at B a solid phase is present, as shown by the kink in the curve. In other words we have struck the boundary curve along which tin and the phase, called by Heycock and Neville AuCd, are the solid phases. Further additions

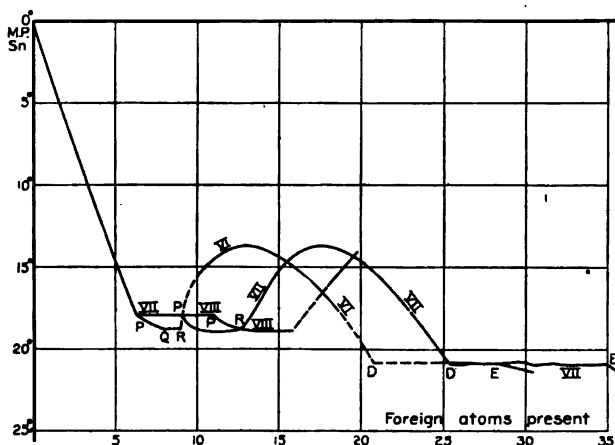


Fig. 3

of cadmium will carry us along the boundary curve until at D we strike the quintuple point, where AuCd, Sn, and a phase, which we shall show to be AuCd<sub>3</sub>, are in equilibrium with the melt and vapor. At this quintuple point AuCd changes to AuCd<sub>3</sub>, and further additions of cadmium will carry the system along the boundary curve beyond E. Curves IV-IX show a maximum at the point where gold and cadmium are present in equivalent proportions, while curves II and III do not show such a maximum. We shall find the explanation of this later.

We have seen that the point B in Heycock and Neville's curves is a point on the boundary curve along which AuCd and Sn are the solid phases. If then we plot the concentrations of these points, we should be able to reproduce the boundary curve. These are plotted in Fig. 4. The ordinates are atoms

cadmium per hundred atoms tin and the abscissæ are atoms gold per hundred atoms tin. On curve III the second phase AuCd appears just after the addition of three atoms of cadmium to three of gold. The minimum at a total of 6.4 atoms of gold and cadmium is without doubt experimental error. From curve II we see that the phase AuCd did not appear (the solution was unsaturated with respect to AuCd) until after the ratio of gold to cadmium had become less than unity; consequently this curve does not show a maximum temperature.

Curve IV shows the temperature of the quintuple point where AuCd, AuCd<sub>3</sub>, Sn, liquid and vapor are solid phases to be 20.9°. Curves VI and VII also show this point, which is the cause of the flat DE. Curve IX, where the gold is being added in excess, and is the solid phase, gives us the temperature of a new quintuple point  $\alpha$  at 18.74°. Quintuple point  $\alpha$  is the point for Au, AuCd, Sn, liquid and vapor. We can read, from the data thus far supplied the location of the boundary curve AuCd, Sn and further from curves VI, VII, and VIII the eutectic for gold and tin at 6.61 atoms of gold per hundred of tin, a temperature of 18.05°. So far as the curves go they give no clue to the composition of the melt at the quintuple points  $\alpha$  and  $\beta$ .

The method by which we find the location of the boundary curve along which AuCd and Sn are solid phases has already been given. Let us next consider how we may determine the composition of the melt at the quintuple points. The first way which suggests itself is that of plotting the boundary curve  $\alpha\beta$ , using atoms cadmium as ordinates and temperatures as abscissæ, and of extrapolating the boundary curve to the temperature 18.74°. We could then read off the number of atoms of cadmium in the melt when the temperature of the quintuple point was reached. Then, by a similar process, plotting gold against temperature we could determine the atoms of gold present at the temperature 18.74° and thereby we shall have determined the concentration of the quintuple point. This method, like all methods involving extrapolation, is liable to be inaccurate. By such an extrapolation the concentration of  $\alpha$  was determined at Au 5.65, Cd 1.53, Sn 100.

Another way to find this point is from curves VI-IX. On curve IX, the temperature of this quintuple point is first noticed when the concentration of cadmium reaches 4, and that of gold 8.38.

In other words, AuCd has been the permanent solid phase until this concentration was reached. Beyond this gold is also present and the thermometer registers only the temperature of the quintuple point. The reason for this lies in the fact that there is another boundary curve  $a\Delta$ , which must rise rather abruptly from  $a$ . Therefore as the gold content of the alloy increases, there must come a concentration such that, on cooling the melt, the concentration strikes the curve  $a\Delta$ . After reaching the curve  $a\Delta$  the concentration will progress to  $a$  and both gold and AuCd will be present as solid phase. The conditions under which Heycock and Neville worked were such that they would not detect this boundary curve  $a\Delta$ , but would always have both Au and AuCd as solid phases, in the region  $abc$ . Since concentration Cd 4 Au 8.31 is the last concentration in the AuCd field to strike the boundary curve  $a\beta$ , it follows that a line at  $45^\circ$  through this concentration will pass through the quintuple point. Similar concentrations taken from curves VI and VIII are Au 6.61, Cd 2.42, and Au 11.0, Cd 5.8. In a similar way the concentrations where Au and Sn are to be solid phases are found to be Au 6.61, Cd 1.46, and Au 11.0, Cd 16.0. These last points should all lie on the same straight line parallel to the gold axis, while those where AuCd and Au are solid phases should all lie on the same straight line, which drawn at  $45^\circ$  should pass through the quintuple point. The intersection of these two lines gives the location of the quintuple point. Determined by this method its concentration is Au 5.7-6.1, Cd 1.5, Sn 100, which agrees closely with the value determined by extrapolation, namely, Au 5.6, Cd 1.5, Sn 100. When we consider how much solid phase was present when these measurements were made, the result is very satisfactory. Two methods of determining the concentration of the quintuple point have been suggested.

The location of the quintuple point  $\text{AuCd}_3$ ,  $\text{AuCd}$ ,  $\text{Sn}$ , liquid and vapor, is quite difficult, owing to the scarcity of data. From extrapolation along the boundary curve we find  $\beta$  to be at  $\text{Au } 0.7$ ,  $\text{Cd } 11.25$ ,  $\text{Sn } 100$ . The gold content is probably higher than this and the cadmium a little less. From curves II, III, IV, and VI we would locate the composition of  $\beta$  at about  $\text{Au } 1$ ,  $\text{Cd } 10$ ,  $\text{Sn } 100$ . But this can be regarded only as an approximate figure.

We have been able to locate the boundary curve along which  $\text{AuCd}$  and  $\text{Sn}$  are solid phases. We have shown how to locate the composition of the quintuple point and have located one with considerable accuracy.

In the diagram (Fig. 4) there would be a boundary curve  $\alpha\gamma$  along which gold and tin were the solid phases, but only points  $\alpha$  and  $\gamma$  are known. From  $\alpha$  there would also be the boundary curve  $\alpha\Delta$ , along which gold and  $\text{AuCd}$  would be the solid phases, but it probably rises pretty rapidly from the quintuple point. We have no data to show which direction it would move, with respect to the axes, but it would in general move up and to the right.

At the quintuple point  $\beta$  there are in equilibrium  $\text{AuCd}_3$ ,  $\text{AuCd}$ ,  $\text{Sn}$ , liquid and vapor. In addition to the boundary curve  $\text{AuCd}$ ,  $\text{Sn}$ , there must be one for  $\text{AuCd}_3$ ,  $\text{Sn}$  ( $\beta h$ ) and  $\text{AuCd}$  ( $\beta g$ ),  $\text{AuCd}_3$ , but there are no data to show the directions which they take.

In Fig. 4 the following fields are thus found to exist. In the field lying between the axes and the boundary curves  $\gamma\alpha\beta$  is the field in which tin is the solid phase in equilibrium with the melt. To the right of the curve  $\alpha\gamma$  gold is the solid phase. In the field  $ba\beta j$ ,  $\text{AuCd}$  is the solid phase. In the triangular portion  $abc$  the solution is saturated with respect to both  $\text{AuCd}$  and  $\text{Au}$  at the temperature of the experiments and both are present as solid phases. Similarly in a triangular region  $j\beta i$  both  $\text{AuCd}_3$  and  $\text{AuCd}$  are present as solid phases at all temperatures covered by Heycock and Neville's experiments.

If we are right as to the phases in these fields we can go



further and tell something of what happens during the cooling of concentrations within the range of this diagram. For example, since tin is the solid phase in the region between  $\gamma a B \beta$  and the axes, it follows that alloys in this field will on freezing change concentration along a straight line drawn through the origin and the point representing their initial concentration. If

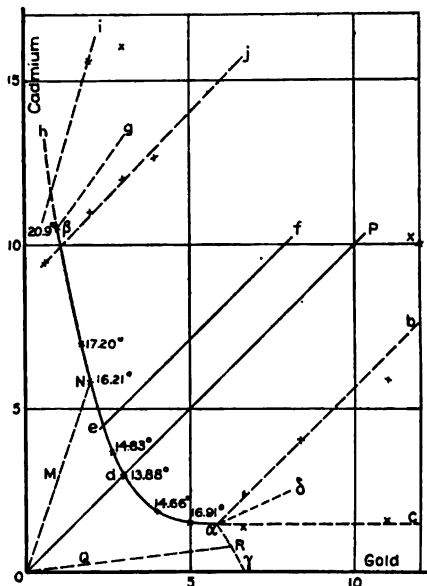


Fig. 4

this line strikes the boundary curve a second break in the cooling curve would appear when AuCd began to separate with the tin, e. g. MN. A concentration as at point Q would begin depositing tin at Q and the second solid phase to appear would be gold which would be present at R.

In the field marked Au, gold is the solid phase and crystallization takes place following to the left a line parallel to the gold axis until tin appears when the melt of such an alloy has reached a composition represented by some point on  $a\gamma$ .

The region  $abc$  is not a field, i. e. Au and AuCd are not stable in contact with the melt having the composition of the points lying within this triangle, but represents a range of con-

centrations at which *at the temperature of these measurements* both AuCd and Au were present.

The composition of the melt was always so near that of the quintuple point that on cooling the only point detected by their thermometers would be the quintuple point. That is, above the line *ab* AuCd alone is present. Below *ac*, gold is in excess and within the area *abc* both are present. This means that so long as the concentration remains in the area *abc* they would always get the same temperature of freezing, namely, that of the quintuple point, and this temperature would remain unchanged whether gold or cadmium was added, as has been explained.

The reason for the existence of this area is that there is a third boundary curve *aΔ* which must rise rather abruptly from *a*. What direction it will take is unknown, all we can say is that if both gold and AuCd crystallize along this curve with falling temperature, then it will lie between the lines *ab* and *ac*, while if gold dissolves and AuCd precipitates it will lie to the left of *ab*, and if AuCd dissolves and Au precipitates, it will lie below *ac*. The way in which this can be predicted will appear in a forthcoming paper from this laboratory.

In the field for AuCd, the change of concentration of the melt would be expressed by a line drawn through the initial composition and at  $45^\circ$  to the axes. That is to say, a change such that the ratio of the concentration of gold to cadmium in the solid phase should be 1:1. Such are the lines OP and AB. The line O*d*P has the further quality that as it is the line connecting the compositions of the solid phases which are in equilibrium along the boundary curve *aβ*, the point at which it cuts the boundary curve will be a maximum temperature for that curve. Therefore all compositions lying on this line OP will on cooling down strike the boundary curve at the same temperature, i. e.  $13.88^\circ$ . This then is the reason that Heycock and Neville found always a minimum fall, when gold and cadmium were present in the alloy in equivalent proportions. The exact location of the triangular area where both AuCd<sub>3</sub> and AuCd are present has not been determined very carefully and only an approximate idea of its position can be had.

Turning again to the curves, Figs. 1, 2, and 3, we are now in a position to understand all of their irregularities. Curves II and III present no difficulties, the point B is the point where the concentration reaches that of the boundary curve  $a\beta$ . Break D shows where the composition enters the region for AuCd and  $\text{AuCd}_3$ , with tin just beginning to separate. Curve II cuts through the narrowest part of this area and the flat DE is correspondingly short. Curve III cuts through at a broader part and the flat is correspondingly longer; as soon as this region is crossed the temperature falls again as we pass along the boundary curve for  $\text{AuCd}_3$  and Sn. The same reasoning accounts for the flat DE of curves IV, VI, and VII. Curve IX after passing the maximum is moving in the opposite direction, gold being increased and cadmium held constant; so that it soon reaches the quintuple point  $a$ , and a further addition of gold merely carries us farther into the region  $abc$  and produces no change of temperature. The last point, where Heycock and Neville added cadmium, has merely carried the concentration out of the area  $abc$  into the field for AuCd and the temperature rises because they pick up the temperature of the boundary curve again. The first flat PQR of curves VI, VII, and VIII now finds a simple explanation in that they added gold until the tin was saturated and the composition of the melt reach the quadruple point  $\gamma$ . The addition of cadmium now caused a fall of temperature following the boundary curve  $\gamma a$ . When  $a$  was reached, additions of cadmium would produce no further change until enough had been added to use up the excess gold to form AuCd. After this the composition was that inside the field AuCd and further additions of cadmium would cause the observed temperature to follow along the boundary curve passing through the maximum and over until at D the new phase  $\text{AuCd}_3$  began to appear. Having thus accounted for the form of the curves obtained by Heycock and Neville, it is next in order to show that the phases are AuCd and  $\text{AuCd}_3$ . This we can do by means of the method suggested by Professor Bancroft.

One way to apply this method is to follow the cooling

curve of an alloy of a certain composition and determine the temperature of the boundary curve. Then remelt the alloy and add either the solid phase, or its components in the ratio in which they are thought to exist in the solid phase. The temperature of the boundary curve is redetermined, and if these two temperatures are the same we have added the solid phase which separates in this field.

This may also be expressed as follows. If two solutions belonging in the same field reach the same boundary curve at the same temperature, the line passing through the points representing the original concentrations must also pass through the point corresponding to the composition of the solid phase which separates. Since the ratio of the concentration changes is the ratio of the two components in the solid phase, the differences in concentration of the second component must be constant, if we compare at the temperatures of the boundary curve two solutions which differ by a constant amount of the first component.

In Heycock and Neville's experiments, they usually held the concentration of gold constant and determined the temperatures at which the boundary curve was reached when varying amounts of cadmium were added. If we take two series of solutions, in each of which the amount of gold is kept constant, the difference in the gold content is necessarily also constant. If we compare the cadmium content of the first series of solutions at a number of temperatures with the cadmium content of the second series of solutions at the same temperatures, we must get a constant difference equal in value to the difference of the gold concentrations if the compound is AuCd. This must be so because the ratio of the gold differences to the cadmium differences must be the same as the ratio of gold to cadmium in the compound and because the gold differences are constant under the method of experimenting adopted by Heycock and Neville. Replotting their curves on a large scale and reading off the concentrations we obtain Table I.

Temperatures are read as degrees below the freezing-point of tin. The Roman numerals give the number of the curves,

and at the right is given the ratio of gold to cadmium as deduced from a comparison of the curves.

TABLE I.

Fall	15.5°	16°	17°	18°	19°	20°	20.7°		
III	6.60	7.29	8.15	9.17	9.93	10.78	11.35	Au 3.00	
II	5.36	5.95	7.00	8.09	8.86	9.75	10.34	Au 2.00	AuCd <sub>1.12</sub>
Diff.	1.24	1.34	1.15	1.06	1.07	1.03	1.01	1.00	Mean 1.12

Fall	15.5°	16°	17°	18°	19°	20°			
IV	7.03	7.58	8.62	9.55	10.39	11.15		Au 3.97	
II	5.36	5.95	7.06	8.09	8.86	9.75		Au 2.00	AuCd <sub>0.78</sub>
Diff.	1.67	1.63	1.56	1.46	1.53	1.40		1.97	Mean 1.54

Fall	15.5°	16°	17°	18°	19°	20°			
VI	9.80	10.38	11.38	12.24	13.01	13.78		Au 6.61	
II	5.36	5.95	7.06	8.09	8.86	9.75		Au 2.00	AuCd <sub>0.92</sub>
Diff.	4.44	4.43	4.32	4.15	4.15	4.03		4.61	Mean 4.25

Fall	15.5°	16°	17°	18°	19°	20°			
VII	12.00	12.50	13.46	14.33	15.09	15.81		Au 9.00	
II	5.36	5.95	7.06	8.09	8.86	9.75		Au 2.00	AuCd <sub>0.9</sub>
Diff.	6.64	6.55	6.40	6.24	6.23	6.06		7.00	Mean 6.35

Fall	15°	16°	17°	18°	19°	20°			
VI	9.19	10.38	11.38	12.24	13.01	13.78		Au 9.00	
III	5.85	7.18	8.15	9.07	9.92	10.78		Au 3.00	AuCd <sub>0.87</sub>
Diff.	3.34	3.20	3.23	3.17	3.09	3.00		3.61	Mean 3.17

TABLE I.—(Continued).

Fall	15°	16°	17°	18°	19°	20°			
VII	11.32	12.50	13.46	14.33	15.09	15.81		Au 9.00	
III	5.85	7.18	8.15	9.07	9.92	10.78		Au 3.00	AuCd <sub>0.87</sub>
Diff.	5.47	5.32	5.31	5.26	5.17	5.03		6.00	Mean 5.24

Fall	14.5°	14°			
V	3.25	4.25	Au 5.00		
IV	2.10	3.53	Au 3.97	AuCd <sub>0.96</sub>	
Diff.	1.25	0.72	1.03		

Fall	14.5°	14°	14°	14.5°	15°	16°	17°	18°	19°	20°
VI	4.79	5.61	7.39	8.49	9.19	10.38	11.38	12.24	13.01	13.78
IV	2.10	3.53	4.44	5.53	6.35	7.53	8.63	9.53	10.39	11.14
Diff.	2.69	2.08	2.95	2.96	2.84	2.85	2.75	2.71	2.62	2.64

Au 6.61		
Au 3.97		AuCd <sub>1.02</sub>
2.64		Mean 2.71

Fall	14.5°	14°	14°	14.5°	15°	16°	17°	18°	19°	20°
VII	6.91	7.70	9.55	10.55	11.32	12.50	13.46	14.33	15.09	15.81
IV	2.10	3.53	4.44	5.53	6.35	7.53	8.63	9.53	10.39	11.14
Diff.	4.81	4.17	5.11	5.02	4.97	4.97	4.83	4.80	.70	4.67

Au 9.00		
Au 3.97		AuCd <sub>0.91</sub>
5.03		Mean 4.60

Fall	15.5°	16°	14°		
VI	3.69	4.20	5.59	Au 6.61	AuCd <sub>0.89</sub>
V	2.31	2.71	4.20	Au 5.00	
Diff.	1.38	1.49	1.39	1.61	

Fall	16.5°	16°	15°	14°			
VII	5.22	5.59	6.40	7.70	Au	9.00	
V	1.71	2.00	2.71	4.20	Au	5.00	AuCd <sub>0.88</sub>
Diff.	3.51	3.59	3.69	3.50		4.00	Mean 3.57

Fall	15.5°	15°	14.5°	14°	15°	16°	17°	18°	19°	20°
VII	5.99	6.40	7.70	9.55	11.32	12.50	13.46	14.33	15.09	15.81
VI	4.14	4.20	5.56	7.39	9.19	10.38	11.38	12.24	13.01	13.78
Diff.	1.85	2.20	2.11	2.16	2.13	2.12	2.08	2.09	2.08	2.03
								Au 9.00 Au 6.61 2.41	AuCd <sub>0.84</sub> Mean 2.08	

On examining these data, we find that within the limits of experimental error the values do agree surprisingly well with the hypothesis that the solid phase to the right of the boundary curve is AuCd. Two points are noticeable however. One is that the ratio runs rather low and that the cadmium differences show in several cases a small but steady decrease. This decrease is in the direction so that it might signify a decrease in the cadmium content of the solid phase as the amount of cadmium in the solution increased. This might happen if tin crystallized with the AuCd, replacing Cd. Heycock and Neville were rather inclined to believe in the existence of such a ternary

compound from analyses made of the precipitate from which as much as possible of the mother-liquor had been pressed out. But such a method is open to the objection that the crystals can never be freed from the mother-liquor. The many compounds of mercury and other metals have been obtained in this way, and mercury hangs less tenaciously to crystals than does molten tin.

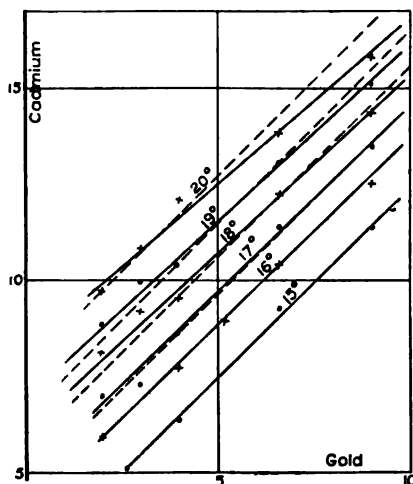


Fig. 5

There is, however, another way of checking this point. If we consider the graphical mean of these results we can tell more nearly whether we are dealing with a ternary compound, a solid solution or experimental error. If in the rectangular diagram (Fig. 5) we plot cadmium as ordinates and gold as abscissæ; and if we plot the concentration of gold and cadmium for each curve at the same temperature, these points should all lie on the same straight line, whose pitch should be  $45^\circ$  to the axes if  $\text{AuCd}$  is the solid phase. If not, the lines for different temperatures will intersect and the point of intersection should give the composition of the solid phase. If all meet in the same point it is a ternary compound. If they show a regular variation, it is a solid solution.

In Fig. 5 the dotted lines are lines drawn at  $45^\circ$ , while the



solid lines are those indicated by the points concentrations of gold and cadmium. It is seen that the lines for all but  $20^\circ$  are very nearly  $45^\circ$  lines. The curves at  $20^\circ$  are pretty steep and the experimental error is correspondingly great. Points from curves II and III are always off the  $45^\circ$  line and in a manner suggesting that these curves had not been determined with the same accuracy as the others. We could check this by the  $20.9^\circ$  break, but in making the readings the thermometer was changed before this point was reached. Let us consider that the lines are not parallel and solve for their intersection

$$\begin{array}{ll} 18^\circ-20^\circ \text{ lines intersection } \text{Au}_{23}\text{Cd}_{27}\text{Sn}_{100} \text{ about } \text{AuCdSn}_4 \\ 16^\circ-20^\circ \text{ " " " } \text{Au}_{38}\text{Cd}_{37}\text{Sn}_{100} \text{ about } \text{AuCdSn}_3. \end{array}$$

The curves for  $15^\circ$ ,  $16^\circ$ ,  $17^\circ$ , and  $18^\circ$  are so nearly  $45^\circ$  lines that their intersection with  $19^\circ$  and  $20^\circ$  would be even further removed and necessitate more tin than  $\text{Sn}_4$ .

The tin content is seen to vary greatly, which indicates that we are not dealing with a ternary compound. So far as these figures go we might have a solid solution. But Heycock and Neville's analysis of the pressed residue which must have contained much more tin (as mother-liquor) than the solid phase found only  $\text{AuCdSn}_2$  as the maximum amount of tin, while these measurements require at least  $\text{AuCdSn}_3$ .

So that from the graphical mean we are led to the conclusion that  $\text{AuCd}$  crystallizes free from tin and the intersection of the plotted lines is due to experimental error. Just how great Heycock and Neville's possible error in temperature might be appears when we recall that these measurements were made with mercury thermometers, read with the eye, and that a large mass of solid was present, rendering it difficult to reach equilibrium. Then, too, the maximum, which is a fixed temperature, varies  $0.12^\circ$ ; the freezing-point of pure tin  $0.16^\circ$ , while the variation they record (for the maximum temperature) bears no relation to the composition of the alloy. This latter should be the case if a solid solution formed. This criticism of the temperature measurements is in no way meant to reflect on the accuracy of the work; but is merely meant to show that the possible error

is enough to account for the slight difference between the found and the theoretical composition of the solid phase.

There is still another way of determining the composition of the solid phase. From any concentration of Au, Cd, and Sn lying in the field where AuCd is the stable phase, draw a line at  $45^\circ$  to the axes and cutting the boundary curve. This line represents the change of concentration of the melt as the phase AuCd crystallizes out. The concentration of the melt at the boundary curve is given by the intersection of this line with the boundary curve. This intersection gives us the atoms cadmium (also gold) present in the melt at the boundary curve. If then we plot the boundary curve from Heycock and Neville's curves (the points and compositions B of the curves) against temperatures, we can read from this the temperature at which a melt containing a number of cadmium or gold atoms of  $b$ , ought to strike the boundary curve. We shall speak of this as the concentration-temperature curve. A concrete case may make this method a little clearer. In Fig. 4, starting with an alloy of composition represented by  $f$ , draw the line  $fe$  through it and at  $45^\circ$  to the axes. The point  $e$  shows the composition of the melt when the alloy  $f$  has cooled down to the temperature of the boundary curve, i. e. where AuCd is the solid phase and Sn is just beginning to crystallize. From the concentration-temperature diagram we can determine the temperature of a melt whose composition is expressed by the point  $e$ . By temperature is meant the temperature at which such a melt strikes the boundary curve. The temperature thus calculated can then be compared with that actually observed by Heycock and Neville. It should be clear that the location of the boundary curve was determined experimentally and is independent of any assumptions as to the composition of the phase called AuCd. If the calculated and observed values agree, it follows that the phase which first crystallized must have changed the concentration of the melt along a line through  $f$  at  $45^\circ$  and consequently the solid phase must contain gold and cadmium in the ratio 1:1. In other words, the solid phase must have the composition AuCd.

If tin crystallized with the AuCd these lines at  $45^\circ$  would not represent the change in concentration of the melt. The true lines would converge, intersecting at the point representing the composition of the solid phase. Supposing such a ternary compound to have a composition expressed by the point  $x$ . The change of concentration on crystallizing would follow the line  $xf$ , the boundary curve being reached at  $yx$ . Since the temperature at  $y$  is very different from that at  $e$ , the temperature calculated on the assumption that the compound was AuCd, and the observed temperature would not agree; while if crystallization followed the line  $fe$  the observed and calculated values would be the same.

The location of the following points (B) taken from Heycock and Neville's curves :

Curve	Atoms Cd	Atoms Au	Temperature
II	5.85	2.00	$16.21^\circ$
III	3.00	3.00	$13.88$
IV	1.83	3.97	$14.66$
V	1.58	5.00	$16.91$
IX	4.00	2.49	$14.63$
X	7.00	1.72	$17.20$

The values in Table II have been derived following the method described. The first column gives the number of the curve, the second (In Cd) the atoms cadmium in the initial solution; and the third (B. C. Cd) give the concentration at which the  $45^\circ$  line through the initial concentration strikes the boundary curve. The fourth column gives the temperature calculated as above, and the fifth the temperature actually observed by Heycock and Neville for that initial concentration. The last column gives the difference between the theoretical and calculated values.

Curves IV, V, and IX give practically an absolute agreement. Curve VI varies as much as seven-tenths of a degree, but there the experimental error is large, or as seen, for Cd 1.64 Heycock and Neville obtain in one case (V)  $15.85^\circ$  and in another (VI)  $15.07^\circ$ , while VII gives for 1.66 Cd  $15.32^\circ$ ; while for Cd = 2.04 the temperature is  $14.41^\circ$ , Cd = 2.12  $14.40^\circ$ , and for

$\text{Cd} = 2.06 \text{ } 14.15^\circ$ . The fact is also to be taken into account that the maximum, which was determined with more care than any other point, varies from  $14.00^\circ$  to  $13.76^\circ$ . This curve VI which places the maximum at  $13.76^\circ$  should be checked before its irregularities are given any great weight. Further the concentration temperature curve is very steep between one and two atoms of cadmium and an error of one-tenth of an atom in the composition of the boundary curve melt can mean at this point nearly a degree difference in temperature. On the other side of the maximum interpolation is more satisfactory. It is also to be remembered that these determinations of Heycock and Neville were not duplicated, so that we feel justified in drawing the conclusion that the solid phase really is  $\text{AuCd}$ , as shown by Tables I and II, and the graphical mean taken in connection with the quantitative analysis of the solid phase.

TABLE II.

Curve	In. Cd	B. C. Cd	Fall calc.	Fall obs.	Difference
IV	2.274	2.045	$14.40^\circ$	$14.41^\circ$	$-0.01^\circ$
	2.625	2.225	14.27	14.25	$+0.02$
	3.104	2.487	14.12	14.10	$+0.02$
	3.709	2.830	14.01	14.01	0.00
	4.308	3.200	13.95	13.88	$+0.07$
	4.469	3.300	14.00	14.05	$-0.05$
	4.988	3.630	14.37	14.32	$+0.05$
	5.493	3.980	14.61	14.49	$+0.12$
	5.986	4.350	14.85	14.75	$+0.10$
	6.483	4.750	15.17	15.08	$+0.09$
	6.963	5.120	15.49	15.47	$+0.02$
	8.095	6.060	16.31	16.55	$-0.14$
V	1.78	1.60	$16.37^\circ$	$16.31^\circ$	$+0.06^\circ$
	2.04	1.64	15.80	15.85	$-0.05$
	2.55	1.75	15.00	15.16	$-0.16$
	3.01	1.90	14.52	14.71	$-0.19$
	3.42	2.12	14.30	14.40	$-0.10$
	3.90	2.35	14.10	14.13	$-0.03$
	4.23	2.53	13.99	13.97	$-0.02$
	4.55	2.72	13.92	13.91	$+0.01$
	4.82	2.87	13.87	13.86	$+0.01$
	5.07	3.00	13.88	13.86	$+0.02$

TABLE II.—(Continued).

Curve	In. Cd	B. C. Cd	Fall calc.	Fall obs.	Difference
VI	3.50	1.64	15.77°	15.07 <sup>01</sup>	+0.70°(?)
	4.58	1.87	14.57	14.60	-0.03
	5.68	2.44	14.05	13.93	+0.12
	6.61	2.97	13.88	13.76 <sup>1</sup>	+0.12 (?)
	7.63	3.60	14.27	14.13	+0.14
	8.54	4.30	14.87	14.48	+0.39
II	7.06	6.82	17.05°	17.01°	+0.04°
III	4.06	3.67	14.32°	14.24°	+0.08°
	4.48	3.95	14.57	14.38	+0.19
	5.07	4.38	14.95	14.58	+0.37
	5.95	5.70	15.57	15.07	+0.50
	7.01	5.97	16.32	15.89	+0.43
	8.16	6.88	17.12	17.06	+0.06
X	1.94	6.82	17.05°	16.99°	+0.06
	2.24	6.57	16.84	16.66	+0.18
	2.46	6.40	16.69	16.45	+0.24
	2.70	6.22	16.53	16.15	+0.38
	4.00	5.15	15.62	15.14	+0.38
VII	6.13	1.66	15.67°	15.32°	+0.35°
	6.69	1.79	14.83	14.68	+0.15
	7.37	2.06	14.35	14.15	+0.20
	7.85	2.33	14.12	13.92	+0.30
	8.43	2.65	13.93	13.81 <sup>2</sup>	+0.11
	8.97	2.96	13.88	13.83	+0.05
	9.49	3.26	14.02	13.99	+0.03
	10.27	3.77	14.41	14.34	+0.06
	11.61	4.80	15.30	15.21	+0.09

<sup>1</sup> See 1.64 of V = 15.85° and max. 0.12° too high.<sup>2</sup> Maximum 0.07 too high. Gold point is 0.3° too high.

TABLE II.—(Continued).

Curve	Atoms Au In. Cd.	B. C. Cd	Fall calc.	Fall obs.	Difference
IX	2.69	3.85	14.50°	14.40°	+0.10°
	2.89	3.71	14.35	14.24	+0.11
	3.09	3.56	14.23	14.13	+0.10
	3.29	3.43	14.14	14.02	+0.12
	3.49	3.31	14.06	13.96	+0.10
	3.71	3.17	13.97	13.92	+0.05
	3.91	3.05	13.90	13.82*	+0.08
	4.12	2.92	13.87	13.82	+0.05
	4.51	2.68	13.92	13.86	+0.06
	5.12	2.35	14.10	14.13	—0.03
	5.92	1.92	14.57	14.57	0.00
	6.48	1.74	15.04	14.89	+0.05
	6.88	1.66	15.65	15.35	+0.30
	7.34	1.59	—	15.97	—
	7.84	1.49	—	16.72	—
	8.35	1.48	18.74	18.74	0.00
	8.38	1.48	18.74	18.74	0.00
	9.40	1.48	18.74	18.74	0.00
	9.96	1.48	18.74	18.74	0.00
	10.49	1.48	18.74	18.74	0.00
	11.02	1.48	18.74	18.74	0.00
	11.52	1.48	18.74	18.74	0.00
	11.94	1.48	18.74	18.74	0.00
	—	1.48	18.74	18.74	0.00
	—	1.48	18.74	18.74	0.00
	—	1.48	18.74	18.74	0.00
	13.98	1.48	18.74	18.74	0.00

On curves II, III, and IV it was pointed out that a new phase appeared beyond E, and it was suggested that this new phase was  $\text{AuCd}_3$ . Although the data are scarce, we have compared these curves with the result shown in Table III.

The cadmium difference is very constant, though showing a slight decrease, but from all the present data the phase may be said to be  $\text{AuCd}_3$ . Unfortunately we cannot in this case plot the boundary curve, nor check the composition graphically, but from the determination of  $\text{AuCd}$  we feel certain that this new phase must be  $\text{AuCd}_3$ .<sup>1</sup>

<sup>1</sup> Mylius and Fromm have already obtained this compound by precipitating gold from its solutions by metallic cadmium.

TABLE III.

Fall	22°	22.5°	23°	23.5°	24°	24.5°	25°		
IV	19.78	20.46	21.08	21.63	22.18	22.73	23.24	Au 3.97	
II	14.08	14.81	15.47	16.08	16.65	17.20	17.75	Au 2.00	AuCd <sub>2.8</sub>
Diff.	5.70	5.65	5.61	5.55	5.53	5.53	5.49	1.97	Mean 5.58

Fall	21.5°	22°	22.5°	23°	24°	25°			
III	16.62	17.35	17.93	18.60	19.76	20.80		Au 3.00	
II	13.30	14.09	14.80	15.45	16.65	17.79		Au 2.00	AuCd <sub>2.16</sub>
Diff.	3.32	3.26	3.13	3.15	3.11	3.01		1.00	Mean 3.16

Fall	22°	22.5°	23°	24.0°	25°				
IV	19.78	20.46	21.08	22.10	23.24			Au 3.97	
III	17.35	17.93	18.60	19.76	20.80			Au 3.00	AuCd <sub>2.5</sub>
Diff.	2.43	2.53	2.48	2.34	2.44			0.97	Mean 2.44

Which again gives a remarkably satisfactory proof that the compound is AuCd.

TABLE V.

Temp.	Au	Cd	Cd/Au
292°	0.8	0.6	0.7
291	1.0	0.9	0.9
290	1.2	1.2	1.0
289	1.4	1.4	1.0
288	1.6	1.6	1.0
287	1.8	1.8	1.0
286	2.0	2.0	1.0
285	2.2	2.1	0.95

In a second paper,<sup>1</sup> a series of determinations are given where Au and Cd, and Ag and Cd are dissolved, in different solvents, and gold and aluminum in tin. Since only one curve is given for all solvents except thallium, lead, and tin, we can use only these for calculating the composition of the solid phase.

<sup>1</sup> Jour. Chem. Soc. 65, 65 (1894).

The determinations of gold and cadmium in lead do not give a very good agreement. The maximum as given by the experimental data varies some  $0.2^\circ$  and the curves I and II (Fig. 6) show evidence of a mistake somewhere. Since in I and II we are approaching the maximum from different sides, we compare the data on the opposite sides of the maximum. It follows, thus, that BC of II should have the same shape and position as AB of I, so that there is something wrong with the determinations. However we may compare over a small range BC I with AB II. The results of this comparison are tabulated in Table IV.

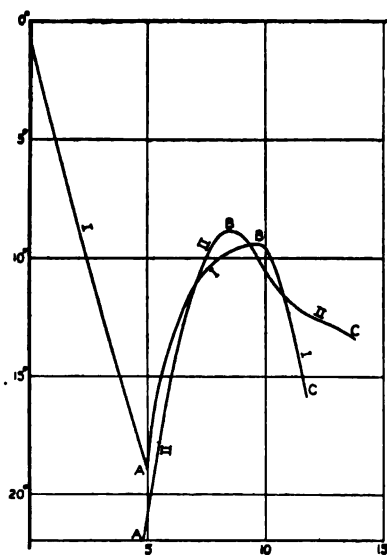


Fig. 6

TABLE IV.

Temp.	Au	Cd	Cd/Au
317°	3.5	3.6	1.03
316	3.2	3.3	1.03
315	2.9	2.9	1.00
314	2.6	2.7	1.03
313	2.4	2.4	1.00
312	2.1	2.2	1.04



In the case of the curve for gold and cadmium dissolved in thallium (Fig. 7) they did not determine the part *xc* of the curves; but if we assume it to be about right as drawn, Table V is obtained.

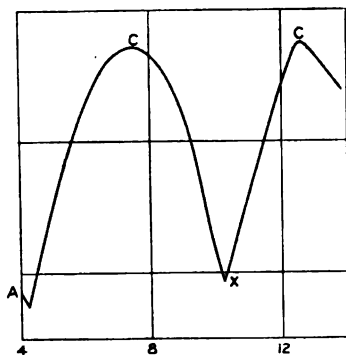


Fig. 7

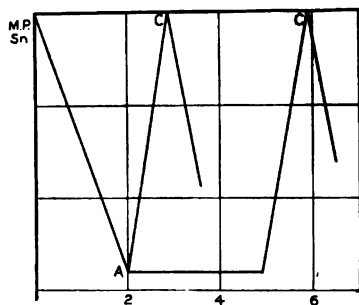


Fig. 8

So that in thallium solution we find again proof of the existence of the compound AuCd. And the method is shown to apply successfully.

In the case of gold and aluminum dissolved in tin (Fig. 8) we find on comparing the curves, the results given in Table VI. as satisfactory a ratio as could be desired.

TABLE VI.

Temp.	229°	230°	231°	231.5°	231°	230°		
X	1.03	1.36	1.69	1.96	2.11	2.45	Al = 4	
IX	0.11	0.42	0.73	0.96	1.10	1.45	Al = 2	
AuX—AuIX	0.92	0.94	0.96	1.00	1.01	0.98	2	Mean Au <sub>0.97</sub>
Ratio Au : Al = Au <sub>0.97</sub> Al <sub>2</sub>								

So far as the compounds AuCd and AuAl<sub>2</sub> are concerned they have both been prepared in the pure state and are definitely settled. The existence of the compound AuCd<sub>3</sub> was not suspected by Heycock and Neville. But the method by which its existence is shown has been tested and found to apply to those cases where the composition of the solid phase was already known. So that we regard the proof as conclusive that a compound AuCd<sub>3</sub> does exist.

However this is not in itself of any importance. The real object of this paper has been rather to call attention to this simple method of determining the composition of the solid phase.

For alloys of the more volatile metals it seems to be the only method whereby we may hope to discover their chemical constitution, and for the much neglected amalgams of the high-melting metals, such as gold, copper, and silver, it should be not only fairly easy of application, but is the only way at present. The same is true of cadmium and to a less extent of zinc alloys. In fact in all cases where the freezing-point curve cannot be determined.

In several places it has been suggested that the determinations of temperature must be in error. But when we remember the conditions under which the measurements were made and that the determinations were not duplicated, the remarkable agreement between the theoretical and observed values is a high tribute to the rare skill of Heycock and Neville for making such measurements.

In conclusion, the writer wishes to express his indebtedness to Prof. Bancroft, by whom the paper was outlined.

*Cornell University*

## A REACTION WHOSE RATE IS DIMINISHED BY RAISING THE TEMPERATURE

BY CLARA C. BENSON

Towards the close of my measurements of the rates of the reactions in solutions containing chromic acid, potassium iodide and ferrous sulphate,<sup>1</sup> I was surprised to find that the amount of iodine liberated in a minute at 30° was less than that set free in the same time at 0° (see Table 24).

Taken by itself, this result does not prove that the rate of liberation of iodine is less at 30° than at 0°, and at first I thought it most likely that at the higher temperature the reaction was over before the minute was up. Analyses at the expiration of two, four and eight minutes, however, showed that, far from being completed within sixty seconds, the reaction was still proceeding after four minutes; and as in blank experiments (no FeSO<sub>4</sub>) no iodine was set free inside of eight minutes, the conclusion is unavoidable that the oxidation of potassium iodide by chromic acid in presence of ferrous sulphate is retarded by raising the temperature.

The measurements detailed in the following tables show that the nature of the reaction at 30° is much the same as at 0°. At the higher temperature, as at the lower, the rate is proportional to the first power of the concentration of the iodide (Tables 24 and 25), to the first power of the concentration of the ferrous salt (Tables 24 and 26) and to the 1.7th power of the concentration of the bichromate (Tables 24 and 27). The retarding influence of the products of oxidation (Tables 24, 28, 34 and 30) is somewhat less at the higher temperature, and its "ageing" (Tables 15 and 29) is more rapid. In experiments carried out without addition of the products of oxidation, the rate is proportional to the fourth power of the concentration of the acid (Tables 31 and 32);

<sup>1</sup> Jour. Phys. Chem. 7, 356 (1903).

while in their presence it varies with the second or third power only (Tables 24, 33 and 34). At zero, in the presence of excess of the products of oxidation the rate is proportional to the fourth power, while in the absence of ferric salts the reaction is too quick for accurate measurement. It is a consequence of this difference in the order of the reaction with respect to the acid, that while in Tables 24, 25, 26 and 27 the reaction is four or five times as quick at  $0^{\circ}$  as at  $30.2^{\circ}$ , in Tables 33 and 34 where larger quantities of the acid were employed, it is seven and fifteen times as quick, respectively.

A single experiment (Table 35) shows that, as was to be expected, the rate of oxidation of ferrous sulphate by chromic acid in absence of potassium iodide is accelerated by heat; Mr. DeLury<sup>1</sup> has found that the same is true for the oxidation of potassium iodide in absence of ferrous salts.

The only reactions hitherto studied whose rates have a negative temperature coefficient, so far as I am aware, are those in which a colloidal catalytic agent is involved; in these cases the rate passes through a maximum as the temperature is increased, and then falls off because of the coagulation of the colloid. In the experiments of the present paper the only colloid present is the ferric salt, and its coagulation, instead of retarding, accelerates the reaction.

It seems probable, however, that as the rates in other complex systems came to be studied, further cases of negative temperature coefficients will be met with, and that the present instance may be regarded as typical of a new class. Both ferro-iodion theory and peroxide theory are ready with an explanation of the retardation; the former by assuming that the amount of  $\text{FeI}^+$  undissociated is less at high temperatures, and the latter by asserting that as the temperature is raised the peroxide reacts more with the residual ferrous salt, and less with the iodide.

I regret that in the time at my disposal I am not able to undertake the large amount of work necessary to ascertain whether either theory could be brought into accord with quan-

<sup>1</sup> Jour. Phys. Chem. 7, 239 (1903).

titative measurements; and at the close of this research I wish to express my sincere thanks to Prof. W. Lash Miller for his interest and assistance.

*The University of Toronto,  
November, 1903.*

The experiments were carried out as described in this Journal, 7, 357, and the abbreviations made use of in these tables are those explained in that paper.

*Ac*, 10 represents ten cc of 0.059*F* sulphuric acid (0.059 gram-formula-weights  $H_2SO_4$  per liter); *Cr*, 10, ten cc of 0.0083*F*  $K_2Cr_2O_7$  (including unreduced bichromate in the "*Ox*"); *KI*, 10, ten cc of 0.0479*F* *KI*; *Fe*, 1.0, one cc of 0.05*F* ferrous sulphate; *Ox*, 5, the product of oxidation of five cc of 0.05*F* ferrous sulphate;  $\theta$  is the duration of the reaction in minutes; *As*, the number of cc of  $n/100$  sodium arsenite equivalent to the iodine liberated; *V*, the total volume in cc of the reacting mixture.

For the sake of convenience, the tables are numbered consecutively with those of the previous paper, "*As*, 0° (Table 3)," for example, referring to Table 3, Jour. Phys. Chem. 7, 379.

I take this opportunity of correcting the following misprints: Table 22 (Jour. Phys. Chem. 7, 387), second column, should read: 100, 129, 152, 162, in place of 100, 116, 126, 131. In equation 7 (p. 372) the sign of equality has been omitted after  $dy/d\theta$ , and on page 376 the / sign has been omitted from the expression  $a^2/k(1-a) = 1077$ .

TABLE 24

*Ac*, 10; *Cr*, 20; *KI*, 20; *Ox*, 5; *Fe*, 1.0; *V*, 700

$\theta$	0.5	1	2	4	8
<i>As</i> , 30.2° (Expt. 37)	—	0.55	1.05	1.80	2.40
<i>As</i> , 0° (Table 3)	1.05	1.90	3.10	4.30	5.60

Blanks (30.2°):  $\theta = 4$ , *As* = 0;  $\theta = 8$ , *As* = 0.45

TABLE 25

Ac, 10; Cr, 20; KI, 10; Ox, 5; Fe, 1.0; V, 700

$\theta$	1	2	4	8
As, 30.2° (Expt. 38)	—	0.80	1.10	1.85
As 0° (Table 8)	1.40	2.20	3.30	4.30

Blank (30.2°):  $\theta = 8$ ; As = 0

TABLE 26

Ac, 10; Cr, 20; KI, 20; Ox, 5; Fe, 0.5; V, 700

$\theta$	1	2	4	8
As, 30.2° (Expt. 39)	—	0.55	0.90	1.45
As, 0° (Table 3)	1.00	1.75	2.50	3.30

Blanks (30.2°):  $\theta = 4$ , As = 0;  $\theta = 8$ , As = 0.45

TABLE 27

Ac, 10; Cr, 30; KI, 20; Ox, 5; Fe, 1.0; V, 700

$\theta$	0.5	1	2	4	8
As, 30.2° (Expt. 40)	—	0.80	1.45	2.30	2.80
As, 0° (Table 6)	1.75	2.95	4.15	5.30	—

Blanks (30.2°):  $\theta = 5$ , As = 0;  $\theta = 8$ ; As = 0.60

TABLE 28

Ac, 10; Cr, 20; KI, 20; Ox, 0; Fe, 1.0; V, 700

$\theta$	0.5	1	2	4	8
As, 30.2° (Expt. 41)	0.90	1.45	1.80	2.30	2.60
As, 0° (Table 12)	3.95	5.00	5.85	6.30	—

Blank (30.2°):  $\theta = 8$ , As = 0

TABLE 29

Expt. 42. Ac, 10; Cr, 20; KI, 10; Ox, 5; Fe, 1.0; V, 700;  
Temp. 30.2° C

Age of Ox	fresh	fresh	3 days	3 days
$\theta$	2	4	2	4
As	0.80	1.10	1.10	1.35

TABLE 30

Expt. 43. Ac, 20; Cr, 20; KI, 20; Ox, 0; Fe, 1.0; V, 700;  
Temp. 30.2° C

$\theta$	0.25	0.5	1.0
As	2.65	3.40	4.40

TABLE 31

Expt. 44. Ac, 10; Cr, 10; KI, 20; Ox, 0; Fe, 1.0; V, 700;  
Temp. 39.7° C

$\theta$	2	4	8	16
As	0.30	1.10	1.35	2.25

TABLE 32

Expt. 45. Ac, 20; Cr, 10; KI, 20; Ox, 0; Fe, 1.0; V, 700;  
Temp. 39.7° C

$\theta$	0.5	1	2
As	1.40	2.15	2.70

TABLE 33

Ac, 15; Cr, 20; KI, 20; Ox, 5; Fe, 1.0; V, 700

$\theta$	0.5	1	2
As, 30.2° (Expt. 46)	0.55	1.15	2.00
As, 0° (Table 5)	3.00	4.60	6.00

TABLE 34

Ac, 20; Cr, 20; KI, 20; Ox, 5; Fe, 1.0; V, 700.

$\theta$	0.25	0.5	1	2	4
As, 30.2° (Expt. 47)	—	1.35	2.25	3.40	4.30
As, 0° (Table 5)	4.05	5.75	7.15	8.00	—

Blank (30.2°):  $\theta = 4$ , As = 0

TABLE 35 (Expt. 48)

In the mixture Ac = 20, Cr = 10, Ox = 5, Fe = 1.0, V = 700, at 0°, after half a minute, 0.78 cc of the ferrous salt remained unoxidized (Table 19).

In the same mixture at 30.2°, the amount of ferrous sulphate remaining after half a minute caused the liberation (in four minutes) of iodine equivalent to As = 1.15, when KI = 20 was added, and water enough to bring the total volume up to 800 cc.

But in the mixture Ac = 20, Cr = 10, KI = 20, Ox = 5, Fe = 0.75, V = 800, for  $\theta = 4$ , As = 1.70. Consequently, less than 0.75 cc of FeSO<sub>4</sub> must have remained unoxidized after half a minute in the previous experiment (See Jour. Phys. Chem. 7, 1 (1903)).

## LIST OF EXPERIMENTS

Expt.	Table	Ac	Cr	KI	Ox	Fe	Temp.	Page	
1	1	10	10	20	5	1	0°	378	See also Tables 16, 17
2	1	10	10	20	5	0.5	0°	378	" " " 17
3	2	15	10	20	5	1	0°	378	
4	2	15	10	20	5	0.5	0°	378	
5	3	10	20	20	5	1	0°	379	" " " 16, 17
6	3	10	20	20	5	0.5	0°	379	" " " 17
7	4	20	10	20	5	1	0°	379	
8	4	20	10	20	5	0.5	0°	379	
9	5	20	20	20	5	1	0°	380	" " " 16, 17
10	5	15	30	20	5	1	0°	380	
11	5	15	20	20	5	1	0°	380	
12	6	10	30	20	5	1	0°	380	
13	6	10	30	20	5	0.5	0°	380	
14	7	10	20	5	5	1	0°	381	" " " 16, 17
15	7	10	20	5	5	0.5	0°	381	" " " 17
16	8	10	20	10	5	1	0°	381	" " " 16, 17
17	8	10	20	10	5	0.5	0°	381	" " " 17
18	9	10	20	30	5	1	0°	382	
19	9	10	20	30	5	0.5	0°	382	
20	10	10	20	20	5	2	0°	382	
21	10	10	20	20	5	1.5	0°	382	
22	10	20	10	20	5	0.25	0°	382	
23	12	10	20	20	0	1	0°	383	" " " 16, 17
24	12	10	20	20	2.5	1	0°	383	
25	12	10	20	20	3.3	1	0°	383	
26	12	10	20	20	5.0	1	0°	383	
27	12	10	20	20	10	1	0°	383	
28	13	10	20	20	0	1	0°	384	K <sub>2</sub> SO <sub>4</sub> added
29	13	10	20	20	0	1	0°	384	Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> added
30	13	10	20	20	5	1	0°	384	Iodine added
31	13	20	10	20	5	0	0°	384	Haemoglobin added
32	13	10	20	20	0	0	0°	384	Ferrosomatose added
33	13	10	20	20	0	0	0°	384	K <sub>4</sub> Fe(CN) <sub>6</sub> added
—	15	10	20	20	age	1	0°	384	
34	19	10	10	0	5	1	0°	386	
35	19	10	20	0	5	1	0°	386	See also Table 17
36	19	20	10	0	5	1	0°	386	
37	24	10	20	20	5	1	30.2	118	
38	25	10	20	10	5	1	30.2	119	
39	26	10	20	20	5	0.5	30.2	119	
40	27	10	30	20	5	1	30.2	119	
41	28	10	20	20	0	1	30.2	119	
42	29	10	20	10	age	1	30.2	119	
43	30	20	20	20	0	1	30.2	119	
44	31	10	10	20	0	1	39.7	120	
45	32	20	10	20	0	1	39.7	120	
46	33	15	20	20	5	1	30.2	120	
47	34	20	20	20	5	1	30.2	120	
48	35	20	10	20	5	0.75	30.2	120	



## THE DIELECTRIC CONSTANTS OF SOME INORGANIC SOLVENTS<sup>1</sup>

BY HERMAN SCHLUNDT

About four years ago I commenced the study of the dielectric constants of pure solvents. The work was undertaken at the suggestion of Professor Kahlenberg, and was carried out in the Laboratory of Physical Chemistry of the University of Wisconsin. The results obtained appeared in two numbers of the *Journal of Physical Chemistry*,<sup>2</sup> and in complete form as a *Bulletin*<sup>3</sup> of the University of Wisconsin.

The values of the dielectric constants of about sixty pure solvents were determined. The results obtained enabled me to point out some new relations existing between this physical constant and the constitution of the compounds investigated. Moreover, as the ionizing power of a large number of solvents chosen for the measurements had been studied by Kahlenberg and Lincoln,<sup>4</sup> Lincoln,<sup>5</sup> and Walden,<sup>6</sup> the results had a special bearing on the Nernst-Thomson rule, according to which a close parallelism exists between the dissociating power of solvents and their dielectric constants. A number of exceptions to the rule were pointed out, and a number of new examples were found which followed the rule. The inorganic solvents studied followed the rule in a general way, although the parallelism between the ionizing power and the dielectric constant was far from close in several instances.

The dissociating power of inorganic solvents has been dili-

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<sup>1</sup> An abstract of this paper was presented before Section C of the A. A. A. S. on Dec. 31, 1903.

<sup>2</sup> *Jour. Phys. Chem.* 5, 157, 503 (1901).

<sup>3</sup> *Science Series*, Vol. II, No. 6, pp. 353-389 (1901).

<sup>4</sup> *Jour. Phys. Chem.* 3, 12 (1899).

<sup>5</sup> *Ibid.* 3, 457 (1899).

<sup>6</sup> *Ber. chem. Ges. Berlin*, 32, 2862 (1899); *Zeit. anorg. Chem.* 25, 209 (1900).

gently studied since the appearance of my results, by Walden and his pupils.<sup>1</sup> Frankland and Farmer<sup>2</sup> have made a thorough study of the solvent and ionizing power of liquid nitrogen tetroxide. The dielectric constants of the solvents studied by these investigators have, for the most part, not been determined. In view of this fact and the importance attached to the relation of the dielectric constants to the ionizing power of solvents, it appeared desirable to continue the study of the dielectric constants of pure solvents.

The present report embraces the results obtained for the dielectric constants of some halogen compounds of phosphorus, arsenic, and antimony. The values found for the dielectric constant of phosphorus, silicon tetrachloride, and nitrogen tetroxide are also included.

#### **Method and Apparatus**

The dielectric constants were measured by Drude's well-known method.<sup>3</sup> The apparatus used in the former measurements<sup>4</sup> served for this work. A vacuum tube containing hydrogen was used to determine the settings for maximum resonance. This particular tube was selected from a lot of tubes belonging to the Department of Physics. Professor Stewart kindly placed at my disposal his extensive collection of Geissler and other vacuum tubes. I tested about thirty of them, but found none that gave better results than the hydrogen tubes. It was observed that the tubes of uranium glass, and the tubes containing fluorescent solutions were specially sensitive to the oscillations. They responded far more readily than the hydrogen tubes, but it is difficult to judge the position at which maximum resonance occurs.

Two cells of the type used for the measurement of substances having low or medium values for dielectric constants served for condensers. The apparatus was calibrated for each cell for values ranging from 2.26 to 20.5 with the standard

<sup>1</sup> *Zeit. anorg. Chem.* 29, 371 (1902); *Zeit. phys. Chem.* 39, 220 (1901).

<sup>2</sup> *Jour. Chem. Soc.* 79, 1356 (1901).

<sup>3</sup> *Zeit. phys. Chem.* 23, 267 (1897).

<sup>4</sup> *Jour. Phys. Chem.* 5, 157 (1901).

liquids recommended by Drude. The capacities of the cells differed somewhat. Both were used for each of the solvents in making the measurements. The values given below represent the average of the two independent determinations thus obtained. Whenever the two values for any one substance differed from each other by 5 percent or more, the measurements were repeated.

The methods of preparing and rectifying the various solvents will be found under each particular solvent in the statement of results given below. In most cases the specific conductivity of the solvents was measured. The Kohlrausch method for measuring conductivities of electrolytes was followed. The range of the apparatus at my disposal for these measurements was rather limited. Specific conductivities less than  $2 \times 10^{-6}$  could not be determined with accuracy.

#### Experimental Results

*Phosphorus Trichloride.*—The sample used for the measurements was Kahlbaum's preparation. It was redistilled, boiling at  $73.9^{\circ}\text{C}$  under a pressure of 738 mm. The value found for its D. C. at  $18^{\circ}$  was 3.72. This value is somewhat higher than the one obtained when this substance was formerly measured.<sup>1</sup> The present value, 3.72, is probably nearer the truth than the older value of 3.36 at  $22^{\circ}\text{C}$ .

*Phosphorus Tribromide.*—The sample was prepared by dropping bromine slowly on red phosphorus. The crude product was poured off from the red phosphorus remaining and was rectified by several distillations. The sample which served for the measurements had its boiling-point at  $170.5^{\circ}$  under a pressure of 757 mm. Its density at  $20^{\circ}$ , as compared with water at  $4^{\circ}$ , was found to be 2.8856. Its specific conductivity was less than  $1 \times 10^{-6}$ . The value found for its D. C. at  $20^{\circ}$  was 3.88.

*Phosphorus Triiodide.*—This compound was prepared by slowly adding a solution of yellow phosphorus in carbon disulphide to the required amount of iodide dissolved in carbon disul-

<sup>1</sup> Jour. Phys. Chem. 5, 512 (1901).

phide. The greater portion of the carbon disulphide was then distilled off. Upon cooling, crystals of phosphorus triiodide formed in the residual solution. The mother-liquor was poured off, and the crystals dissolved in a fresh portion of carbon disulphide, which was distilled off in part as before. The mother-liquor was again poured off from the crystals, and the adhering solvent removed by warming the crystals to  $40^{\circ}$  under diminished pressure. The red crystals of phosphorus triiodide were protected from coming in contact with moist air. The melting-point was found to be  $55^{\circ}$  C. The D. C. of the solid sample at  $20^{\circ}$  was found to be 3.66. For the liquid at about  $65^{\circ}$  C the value 4.12 was found for the D. C. The positions for maximum resonance were well defined.

*Arsenic Trichloride.* — The D. C. of this compound in the liquid state had been previously measured.<sup>1</sup> Its D. C. was again determined and found to be 12.6 at  $17^{\circ}$ , which agrees fairly well with former value of 12.35 at  $21^{\circ}$ . Kahlbaum's sample was used for the measurements. It was redistilled. Its boiling-point was  $129.3^{\circ}$  under a pressure of 753 mm. Its specific conductivity was  $3.8 \times 10^{-6}$ . The D. C. of the solid compound was found to be 3.6 at about  $-50^{\circ}$  C. To solidify the sample the cell was introduced for a short time into a cooling mixture of solid carbon dioxide and ether kept in a small Dewar test-tube. The temperature of the bath was nearly  $-55^{\circ}$  C. After the cell had assumed the temperature of the bath it was taken out and quickly placed in the apparatus and a setting made. After cooling it again, another setting was made. This operation was repeated until 10 settings were obtained.

*Arsenic Tribromide.* — The sample used for the measurements was Kahlbaum's preparation. It was redistilled under a pressure of 20–22 mm. The melting-point of the crystals was  $31^{\circ}$  C. The liquid had a faint yellow tinge. Its specific conductivity was less than  $2 \times 10^{-6}$ . The value found for the D. C. of the liquid at  $35^{\circ}$  was 8.83. The solid gave the value 3.33 at  $20^{\circ}$ .

<sup>1</sup> Jour. Phys. Chem. 5, 512 (1901).

*Arsenic Triiodide.* — Kahlbaum's sample was recrystallized from benzene. Small red crystals were obtained, whose melting-point was found to be  $146^{\circ}$ . The specific conductivity of the liquid at  $150^{\circ}$  was  $3.1 \times 10^{-6}$ . The value 5.38 at  $18^{\circ}$  was found for the D. C. of the solid sample. The D. C. of the liquid, at about  $150^{\circ}$ , was 7.0.

*Antimony Tribromide.* — The compound was prepared by slowly adding bromine to a quantity of finely powdered antimony somewhat greater than the proportion required by the formula. The product was purified by several distillations. The boiling-point of the sample was  $286.4^{\circ}$  under 736 mm pressure, and its melting-point was  $93^{\circ}$ . The liquid had a slight yellow tinge. The specific conductivity at  $100^{\circ}$  was  $5 \times 10^{-5}$ . The D. C. of the liquid at about  $100^{\circ}$  was 20.9. The solid gave the value 5.05 at  $20^{\circ}$ .

*Antimony Triiodide.* — The sample was prepared by bringing together finely powdered antimony and iodine in small quantities and gently warming. The product was distilled twice. Dark red crystals melting at  $167^{\circ}$  were obtained. The specific conductivity of the liquid at  $175^{\circ}$  was  $1.1 \times 10^{-4}$ . The D. C. of the liquid at about  $175^{\circ}$  was found to be 13.9. For the solid at  $20^{\circ}$  the value 9.1 was found.

*Phosphorus.* — A sample of Kahlbaum's yellow phosphorus which had been kept in the dark was freed from adhering water by means of filter-paper. It was melted under chloroform, and by drawing up about a cubic centimeter of it in a medicine dropper between two layers of chloroform, it was easily transferred to the measuring cells without taking fire. The chloroform rises in the stem of the cell and is removed with a little filter-paper. The D. C. found for the liquid at  $45^{\circ}$  was 3.8. The D. C. of the solid sample at  $19^{\circ}$  was 4.24.

A second sample was prepared by redistilling the Kahlbaum sample. The distillate was collected under water. It was transferred to the cells as before, but it was melted under water instead of chloroform. The water must be carefully removed, as a small quantity of acid is formed in the transfer of the sam-

ple to the cell. The presence of the small amount of acid had no effect on the positions of maximum resonance when the phosphorus was liquid. But upon solidifying, the plates of the cell evidently came in contact with the acid, as the positions for maximum resonance were not well defined. The energy was absorbed in the cell. The fact that an excellent electrolyte was in contact with the plates accounts for this absorption. Upon expelling the water by heating to about  $100^{\circ}$ , the solid sample gave a well defined position for maximum resonance. For the liquid sample at  $45^{\circ}$  the value 3.85 was found for the D. C. The solid at  $20^{\circ}$  had the value 4.02.

By keeping a layer of water a few millimeters in thickness over the liquid phosphorus, it may be cooled to  $20^{\circ}$  without solidifying. The value found for the D. C. of the liquid at  $20^{\circ}$  was the same as the value at  $45^{\circ}$ , which was 3.85.

*Silicon Tetrachloride.* — The sample was prepared by passing dry chlorine over amorphous silicon heated to about  $400^{\circ}$ . The product was redistilled; its boiling-point was  $57.50$  under a pressure of  $749$  mm. The D. C. found, at  $16^{\circ}$ , was 2.40.

*Nitrogen Tetroxide.* — The sample was prepared by heating lead nitrate. The gas was passed through a phosphorus pentoxide tower before it was condensed. The D. C. found for the liquid at  $15^{\circ}$  was 2.56. The liquid was solidified by immersing the cell in a Dewar test-tube containing Thilorier's mixture. The snow-white crystalline mass was probably at  $-40^{\circ}$  C when the settings were made. The D. C. of the solid was 2.60.

One of the samples used for the measurements had a green color. The value of the D. C. was the same as that of the yellow samples. Upon solidifying this sample, the crystals at first had a green tinge, but upon further cooling they became pure white.

### Summary of Results

The foregoing values are summarized in Table I and for more ready comparison of some of the values Table II was prepared.

TABLE I.

Substance	Formula	D. C.	$t^{\circ}$
Phosphorus trichloride	$\text{PCl}_3$	3.72	18
Phosphorus tribromide	$\text{PBr}_3$	3.88	20
Phosphorus triiodide	$\text{PI}_3$	4.12	65
" " solid	"	3.66	20
Arsenic trichloride	$\text{AsCl}_3$	12.6	17
" " solid	"	3.6	-50
Arsenic tribromide	$\text{AsBr}_3$	8.83	35
" " solid	"	3.33	20
Arsenic triiodide	$\text{AsI}_3$	7.0	150
" " solid	"	5.38	18
Antimony tribromide	$\text{SbBr}_3$	20.9	100
" " solid	"	5.05	20
Antimony triiodide	$\text{SbI}_3$	13.9	175
" " solid	"	9.1	20
Phosphorus	$\text{P}_4$	3.85	45
" liquid	"	3.85	20
" solid	"	4.1	20
Silicon tetrachloride	$\text{SiCl}_4$	2.40	16
Nitrogen tetroxide	$\text{N}_2\text{O}_4$	2.56	15
" " solid	"	2.6	-40

TABLE II.

	Trichloride		Tribromide		Triiodide	
	Liquid	Solid	Liquid	Solid	Liquid	Solid
Phosphorus	3.72	—	3.88	—	4.12	3.66
Arsenic	12.5	3.6	8.83	3.33	7.0	5.38
Antimony	33.2 <sup>1</sup>	5.34 <sup>1</sup>	20.9	5.05	13.9	9.1

### Discussion of Results

Table II shows that the value for the dielectric constants of the compounds in the solid state is less than the value for the liquid. This drop in the value occurs upon solidification. The

<sup>1</sup> These values for antimony trichloride are taken from a former paper. Jour. Phys. Chem. 5, 512 (1901).

molecular rearrangement which occurs as the substances solidify has a marked effect on the value of the dielectric constant. Substances which become crystalline in structure upon solidifying generally show a considerable change in value of the dielectric constant. Attention has been called to this fact by other investigators, and the great difference in values of the dielectric constants of ice and water is generally cited as an example. Amorphous substances, as a rule, show no marked change in the value of the dielectric constant upon liquefying.

The ionizing power of most of the solvents in the tables has been studied. Walden<sup>1</sup> found that phosphorus trichloride, phosphorus tribromide, and silicon tetrachloride did not possess ionizing power. These substances have low values for their dielectric constants, and hence follow the Nernst-Thomson rule.

The ionizing power of the trichloride of arsenic has likewise been investigated by Walden,<sup>2</sup> and Tolloczko<sup>3</sup> and Walden have studied the ionizing power of antimony trichloride. Their results show that antimony trichloride is an excellent ionizing agent, and that arsenic trichloride has marked ionizing power. Phosphorus trichloride possesses no ionizing properties. The dielectric constant of antimony trichloride is relatively high; that of phosphorus trichloride is quite low; arsenic trichloride occupies an intermediate position in ionizing properties and in the value of its dielectric constant.

Recently Walden<sup>4</sup> has studied the dissociating power of arsenic tribromide. Tetraethyl-ammonium iodide, when dissolved in arsenic tribromide, yields a solution whose molecular conductivity at a dilution of 500 liters is 19.4 at 33°. The same salt when dissolved in arsenic trichloride has a molecular conductivity of 54.3 at a dilution of 480 liters, at 25°. The dielectric constant of the tribromide was found to be less than the value of the trichloride. These solvents then follow the Nernst-Thomson rule.

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<sup>1</sup> *Zeit. anorg. Chem.* 25, 209 (1900).

<sup>2</sup> *l. c.*

<sup>3</sup> *Zeit. phys. Chem.* 30, 709 (1899).

<sup>4</sup> *Zeit. anorg. Chem.* 39, 380 (1902).



Frankland and Farmer<sup>1</sup> have thoroughly studied the solvent and ionizing power of nitrogen tetroxide. They found that it did not possess ionizing power. The low value of the dielectric constant shows that it follows the Nernst-Thomson rule.

The ionizing power of phosphorus, phosphorus triiodide, arsenic triiodide, antimony triiodide, and antimony tribromide, have to my knowledge, not been investigated. On the basis of the values found for the dielectric constants, phosphorus, phosphorus triiodide, and arsenic triiodide should possess little or no ionizing power according to the Nernst-Thomson rule. Antimony tribromide and antimony triiodide should possess marked ionizing properties.

The value of the dielectric constant of silicon tetrachloride lies between the values of carbon tetrachloride and tin tetrachloride. The values however differ but slightly:—

Carbon tetrachloride	D. C. = 2.18 <sup>2</sup> at 17° C
Silicon       “	2.40   “ 16° C
Germanium   “	?
Tin           “	3.2 <sup>3</sup> “ 22° C

A sample of germanium tetrachloride was not available. Its dielectric constant will probably lie between the values found for the chlorides of silicon and tin.

I desire to express my thanks to Professor O. M. Stewart for placing at my disposal for this work an induction coil belonging to the Department of Physics.

*Chemical Laboratory,  
University of Missouri,  
December, 1903.*

<sup>1</sup> Jour. Chem. Soc. 79, 1356 (1901).

<sup>2</sup> Drude. Zeit. phys. Chem. 23, 309 (1897).

<sup>3</sup> Schlundt. Jour. Phys. Chem. 5, 512 (1901).

## A CORRECTION

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BY FRANK K. CAMERON

In a recent issue of this Journal<sup>1</sup> there is a paper entitled "The Toxic Action of Acids and Salts on Seedlings" of which I was a joint author. It was pointed out that the toxic effect of certain acids on clover seedlings was apparently increased by the presence of potassium salts, and the statement was made, "This is of special interest as being, so far as we are aware, the first instance observed when the addition of a second electrolyte to the solution of another, has not reduced the toxic action."

The statement should not have been made in this way, for, together with Mr. Kearney,<sup>2</sup> I had some time previously described several such instances, when working with lupine seedlings. For instance, it was shown that the addition of sodium carbonate did not change the limit for magnesium sulphate; sodium carbonate and magnesium carbonate did not change the limit for magnesium chloride; and sodium chloride increased the toxic action of either sodium carbonate or sodium sulphate. In the great majority of cases, however, the addition of a second electrolyte does decrease the effect of the first, and the existence of these exceptions to an apparent law, complicates very much a study of phenomena for which no satisfactory explanations or generalizations have yet been proposed.

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<sup>1</sup> Jour. Phys. Chem. 8, 1 (1904).

<sup>2</sup> Report 71, U. S. Department of Agriculture.

## NEW BOOKS

**Lehrbuch der Elektrochemie.** By *Max Le Blanc*. *Dritte vermehrte Auflage.* 14 X 22 cm; pp. viii + 284. Leipzig: Oskar Leiner, 1903. Price: paper, 6 marks. — Le Blanc's Electrochemistry has always been recognized as the best of the smaller books on the subject. The new edition is a very satisfactory one so far as the object of the author is concerned. Much of the most recent work has been incorporated and yet the book is still a small one clearly written. It can be recommended most heartily to those who wish a brief presentation of the electrochemistry of dilute aqueous solutions from a strictly orthodox point of view. This statement of the merits of the book discloses its shortcomings as well. There is no reference to Kahlenberg in the whole volume, and a paragraph on Walden and Centnerzwer covers about all that there is on non-aqueous solutions. In other words the book is good as far as it goes; but its object is to expound a theory and not to set forth the facts.

*Wilder D. Bancroft*

**Le Point critique des Corps Purs.** By *E. Mathias*. 14 X 22 cm; pp. viii + 255. Paris: C. Naud, 1904. Price: paper, 7 francs. — The headings of the chapters are: experiments of Andrews; the phenomenon of Cagniard-Latour; methods of determining the three critical constants; methods giving two critical constants; methods giving one critical constant; calculation of the critical constants; critical constants of pure substances; objections to the univariancy of liquid and vapor; the liquidogenic theories; properties of matter above the temperature at which the meniscus disappears.

The author takes the stand that liquid and vapor constitute a univariant system when in equilibrium. He is therefore opposed to the views of de Heen, Galitzine, and others. On the other hand there is much evidence in favor of the view that liquid and vapor differ for a perceptible time after the meniscus disappears. Since many vapors and consequently many liquids are polymerized to a greater or less extent at the critical temperature, it is only necessary to assume that equilibrium is reached slowly in order to account for all the facts. When we remember that dry ammonium chloride does not dissociate and that dry ammonia does not combine with dry hydrochloric acid, there is nothing improbable in this assumption. It is however an assumption *ad hoc* and should be tested by seeing whether the equilibrium pressure at any temperature is or is not reached practically at once.

*Wilder D. Bancroft*

**Fractional Distillation.** By *Sydney Young*. 13 X 18 cm; pp. xii + 284. New York: The Macmillan Co., 1903. — Every chemist is constantly dealing with the problems of fractional separations. He who would work rationally and successfully by saving time and obtaining trustworthy results must know the theories underlying such separations. Preceding the presentation of such theories there must always be discussed the factors of equilibrium and the energies concerned and the methods of measurement indicated.

In the work under review, Professor Young has treated systematically the

factors which are of importance in fractional distillation, has discussed the theories involved, and has given in detail the most important operations and apparatus employed in boiling and distilling liquids under many kinds of varying conditions. In the preface he has stated: "It is in the hope that the solution of the difficulties which so often occur in carrying out a fractional distillation may be rendered easier, and that the value and economy of highly efficient still-heads in laboratory work may come to be more widely recognized than is generally the case, that this book has been written." The reader is not surprised therefore when he finds a very careful and complete comparison of the various forms of still-heads and dephlegmators and a discussion of their efficiencies. A number of chapters detail the work of the author and his students on the uses of fractional distillation in quantitative analysis. The theory has been presented as of secondary importance; the strongest feature of the work is the number of practical points which every laboratory worker can use.

Some readers may think that many of the tables might have been omitted; that in the two-component systems the extension of the discussion to pressures near the critical would have been advisable; that the work on three components is altogether too limited and that the author might with great advantage have referred to the works of Haustrand, Schreinemakers, Ostwald, and others; that the displacement relations on addition of a third component deserve a place at least as important as the methods of quantitative analysis; that the triangular diagram might have been used frequently, and that the temperature and pressure relations in the dephlegmator and the heat and work terms concerned are well worth detailed treatment.

But every one who reads the book carefully will wish to improve his own methods and test the more modern ones; judged by this standard the book will be a success.

H. R. Carveth

*Cours d'Électricité. By H. Pellat. Tome II. Électrodynamique; Magnétisme; Induction; Mesures Électromagnétiques. 16 × 25 cm; pp. 547. Paris: Gauthier-Villars, 1903.*—The second volume of M. Pellat's handsome treatise naturally retains the characteristics of the first. Logical elegance, mostly of the geometrical kind, is sustained throughout, so that the pages suggest the cultured leisure of a Continental University. Pellat begins with electrodynamics as created by Ampère. For brevity's sake, however, he does not follow Ampère, preferring the shorter route through the famous *electrodynamische Maassbestimmungen* of W. Weber. From the reciprocal properties of magnetic shells and circuits, Laplace's law is deduced in a way quite ingenious, and new to the reviewer. The properties of coils, the magnetic field, magnetic potentials, etc., then follow from very clear-cut and simple reasoning.

The next chapter, on magnets, begins with the loadstone and ends with the electric motor, developing all the important intermediate principles. One misses Fleming's well-known three-finger rule, for by contrast the "observateur de Ampère" is a great bungler; but this may be a question of habit. The treatment, with the exception of a few inevitable and straightforward integrations, is elementary, and the explanation given of magnetic induction and magnetic circuits are good examples of a flawless presentation of these subtle subjects.

The chapter on induction opens with a rigorous demonstration of Neumann's remarkable law, that the work done in deforming or displacing an electric circuit per unit of electricity circulating is the negative electromotive force induced. Similarly careful treatment is given to the section on mutual and self-induction, and the method of deriving Neumann's well-known integral seems to be new. One is rather surprised to find the earth inductor called a "cerceau de Delezenne" and the method referred to Verdet. Interesting features are the statement of Kirchhoff's laws in a way to include self-induction, and the expression for the energy of a magnetic field produced by circuits, with a correction for the heat transformation accompanying the passage of current up to its steady value. In deducing Maxwell's equations for the magnetic field and for its energy the usual notation is unfortunately not adhered to, and one is confused on finding X, Y, Z referring to the magnetic vectors, F, G, H to the electric vectors. The chapter concludes with an interesting discussion of the attraction of non-uniform fields, with a final section on hysteresis.

The chapter on electromotors must be passed over hastily, though it is very complete, giving a full account of circuits with self-induction, resistance, and capacity, branched or not. The beautiful method of imaginaries introduced by Steinmetz is appreciatively summarized, and the imaginary forms of Ohm's and Kirchhoff's laws are explained at length. The chapter closes with a detailed discussion of polyphase transmission and of the transformer.

Electrical oscillation is taken up in the next chapter and treated chiefly with reference to the work of French and allied authors (in particular of Blondlot, Sarazin, and de la Rive), and from this point of view the presentation will be novel and interesting to most American readers; but it is curious to find the electromagnetic theory of light relegated to a note in the appendix.

The final chapter, on electromagnetic measurement, is an endeavor to give a general account of this severe subject from a cultural point of view, without going into the details of a treatise on practical physics; and it must be acknowledged that the result is gratifying. One may refer to the excellent description given of Pierre Curie's experiments on the susceptibility of diamagnetic and paramagnetic substances at different high temperatures. Among the galvanometers described, Weiss's modification of Thomson's galvanometer, and Lippmann's ampere-meter, will be new to most readers. Lippmann's modification of Lorenz's well-known method for the determination of the ohm is exhaustively described. A critical discussion of approved methods for measuring the more important electrical variables closes the chapter. Among other matter, the notes give Potier's elegant deduction of wave motion along a wire, and of the superficial distribution of current density in the case of alternating currents of high frequency.

The book, as a whole, will not fit well into an American curriculum, being too advanced for our more elementary work and too diffuse or insufficiently advanced for our maturer classes; but as a work of reference for the guidance of the instructor it cannot be too highly recommended.

Carl Barus

*Der Stickstoff und seine wichtigsten Verbindungen. By Leopold Spiegel.*

15 × 23 cm; pp. xii + 910. Braunschweig: Friedr. Viewig und Sohn, 1903. Price: paper, 20; bound, 22 marks. — The author has given us a bulky monograph on nitrogen and its compounds. The general divisions are: nitrogen, nitrogen-halogen compounds; nitrogen-oxygen compounds; nitrogen-sulphur compounds; nitrogen-hydrogen compounds; nitrides; nitrogen-phosphorus compounds; nitrogen-carbon compounds; the compounds of nitrogen with silicon, titanium, zirconium, and boron; nitrogen in cyclical compounds; alkaloids; proteids; analytical methods. This bit of work has been well done and it was also worth doing. To get a comprehensive view of a subject, as is done here, is of the greatest value. It is to be hoped that this book will be sufficiently successful financially to make the publisher willing to take chances with similar monographs on other elements. *Wilder D. Bancroft*

**The Iron and Steel Metallurgist and Metallographist.** 16 × 24 cm. Boston: Sauveur and Whiting, 1904. — The Metallographist has ceased to exist and its place is to be taken by The Iron and Steel Metallographist and Metallurgist. "The new magazine will be a monthly publication of approximately one hundred pages of descriptive matter devoted to the Iron Industry in its various branches, including blast-furnace practice, foundry work, steel-making, the treatment of steel, physical and chemical testing, the properties of iron and steel, statistics, etc." *Wilder D. Bancroft*

## REVIEWS

*The object of this department of the Journal is to issue, as promptly as possible critical digests of all Journal articles that bear upon any phase of Physical Chemistry*

### General

A revision of the atomic weight of iron. *G. P. Baxter. Proc. Am. Acad. Sci.* 39, 245 (1903); *Zeit. anorg. Chem.* 38, 232 (1904). — The method was the analysis of ferrous bromide, and the most probable value was 55.871. The analysis of ferric oxide had previously given 55.883 (4, 627). The mean of the two sets 55.877 and 55.88 may therefore be considered as very close to the truth. The effect of the earth's magnetism was shown to be negligible.

W. D. B.

Comparative studies in the periodic system. *G. Rudorf. Zeit. anorg. Chem.* 37, 177 (1903). — The author proposes and discusses a new form of the periodic table. There are to be two short periods, He-F and Ne-Cl; three long periods, A-Br, Kr-I, and Xe-Bi; while radium, thorium, and uranium are all that are known of still another period. The other feature of the new plan is that the periods are discontinuous.

W. D. B.

### One-Component Systems

Vacuum distillation in quartz vessels. *A. Schuller. Zeit. anorg. Chem.* 37, 69 (1903). — Working in a vacuum with quartz vessels, the author has sublimed silver, copper, silver sulphide, and lead sulphide; and has distilled gold and tin. With lead sulphide the sublimation pressure was reached.

W. D. B.

A direct method for determining latent heats of evaporation. *J. C. Brown. Jour. Chem. Soc.* 83, 987 (1903). — The liquid is kept at its boiling-point by a jacket of its own boiling vapor. Portions of the liquid are distilled by an electric current. The watts used are measured carefully and the distillate is weighed.

W. D. B.

The density and coefficient of cubical expansion of ice. *J. H. Vincent. Phil. Trans.* 198A, 463 (1902). — The density of ice is found to be 0.9160 at 0°, which is only one part in ten thousand lower than the mean of Nichols's values for artificial ice. The same specimen of water can however freeze into specimens of ice having different density. For this reason "the use of the Bunsen calorimeter in absolute determinations must be limited to an accuracy of probably about one in one thousand." The coefficient of cubical expansion was found to be 0.000152, which was about four percent lower than that of Plücker and Geissler.

W. D. B.

The red and the yellow mercuric oxides and the mercuric oxychlorides.

*E. P. Schock. Am. Chem. Jour.* 29, 319 (1903). — Yellow mercuric oxide crystallizes in square tablets and the red oxide in monoclinic prisms. The two are therefore distinct though the color test is absolutely unreliable. The fact that the solubility of the two may be made the same by grinding the red form to powder proves nothing as to the identity of the two forms. Above 300° the yellow oxide has much the higher vapor-pressure. Ten oxychlorides are described, but it is by no means certain that they all exist. *W. D. B.*

On the law of the pressure of gases between 75 and 150 millimeters of mercury. *Lord Rayleigh. Phil. Trans.* 198A, 417 (1902). — Reviewed (6, 432) from *Zeit. phys. Chem.* 41, 71 (1902).

Molecular weight determinations at very high temperatures. *W. Nernst. Zeit. Elektrochemie*, 9, 622 (1903). — This is essentially the paper that was read before the New York meeting of the American Electrochemical Society; but the subject is treated in more detail and some new experiments on sulphur and on sulphur dioxide are described. *W. D. B.*

On a determination of the ratio of the specific heats at constant pressure and at constant volume for air and steam. *W. Makower. Phil. Mag.* [6] 5, 226 (1903). — The author repeats the experiments of Lummer and Pringsheim, using a platinum thermometer of small heat capacity in place of a bolometer strip. The results for air are quite consistent, giving a value 1.399, but the results for steam, 1.305, being more difficult to obtain, are less regular. *H. T. B.*

#### Two-Component Systems

Freezing-point curves for some binary mixtures of organic substances, chiefly phenols and amines. *J. C. Philip. Jour. Chem. Soc.* 83, 814 (1903). — Freezing-point curves have been determined for phenol with urea, diphenylamine,  $\alpha$ -naphthylamine, *p*-toluidine and picric acid; for *p*-toluidine with *o*-nitrophenol and  $\alpha$ -naphthol; and for *p*-cresol and aniline. No compounds occur with phenol and diphenylamine, and with *p*-toluidine and *o*-nitrophenol. In all the other cases there is one compound, stable at its melting-point and having a molecular ratio of one to one. The compound of phenol and *p*-toluidine appears to exist in two modifications, one of which crystallizes 1.5° higher than the other. With phenol and  $\alpha$ -naphthylamine, the compound crystallizes with surprising slowness and the freezing-point curves with the components as solid phases can easily be followed below the eutectics. *W. D. B.*

The hydrates and solubility of barium acetate. *J. Walker and W. A. Fyffe. Jour. Chem. Soc.* 83, 173 (1903). — The trihydrate changes to the monohydrate at 24.7° and the anhydrous salt first crystallizes at 41°. The solubility curve for the monohydrate shows a minimum at about 30° and that for the anhydrous salt at about 75°. *W. D. B.*

The solubility curve and the critical curve. *A. Smits. Zeit. Elektrochemie*, 9, 663 (1903). — In most binary systems the solubility curve ends at the melting-point or at the point where two liquid phases appear. If the melting-point of one of the components is high and the critical temperature of the



other low, the solubility curve may cut the critical curve, both curves being unstable between these two temperatures. This has been realized experimentally with ether and anthraquinone, the critical temperatures when solid is present being  $195^{\circ}$  and  $241^{\circ}$ .  
W. D. B.

**Solubility curves of some substances in sulphur dioxide.** *M. Ceninerzwer and I. Teletow. Zeit. Elektrochemie*, 9, 799 (1903). — The authors have made measurements on the solubility of anthracene, anthraquinone and hydroquinone in sulphur dioxide at temperatures running up to the critical. Some of the data refer to the "mean solubility", which is the average concentration of the solute in the liquid and vapor phases under the conditions of the experiment. Since this "mean solubility" varies with the relative volumes of liquid and vapor, the authors have given the approximate values of the ratios of these two volumes in each case. Some of the data refer to actual solubilities in the vapor phase or in the liquid phase. With none of these solutes was there an intersection of the solubility curves with the critical curve, as was found by Smits (preceding review) with anthraquinone and ether.  
W. D. B.

**The solubility curve of sodium tetraborate.** *D. W. Horn and E. M. Van Wagener. Am. Chem. Jour.* 30, 344 (1903). — Poggiale's curves for the solubility of borax show no break where the decahydrate changes to the pentahydrate. New determinations show this to be due to experimental error. The inversion point is at  $60^{\circ}$ – $61^{\circ}$ .  
W. D. B.

**On the solubility of arsenic and its molecular weight in solution.** *L. Bruner and S. Tolloczko. Zeit. anorg. Chem.* 37, 455 (1903). — The authors have determined the solubility curve for crystallized arsenic between  $2^{\circ}$  and  $39.8^{\circ}$ . They have then calculated the heat of solution by means of the van't Hoff formula and find that it agrees with the observed value only if they halve the usual formula of  $As_2O_3$ .  
W. D. B.

**Determination of the composition of chemical compounds without analysis.** *G. Tammann. Zeit. anorg. Chem.* 37, 303 (1903). — From the form of the freezing-point curve and from the temperature-time curve, it is possible to make a very close guess as to the composition of a solid phase. This presupposes that no solid solutions are formed.  
W. D. B.

**The association of a liquid diminished by the presence of another associated liquid.** *H. C. Jones and G. Murray. Am. Chem. Jour.* 30, 193 (1903). — The authors have determined the apparent molecular weights, by the freezing-point method, of binary mixtures of water, formic acid and acetic acid. Since the molecular weights of the solutes in the more concentrated solutions are said to be much less than the molecular weights of these substances when pure, the authors conclude that one associated liquid has a depolymerizing effect on another. Unfortunately the authors have taken values since discarded by Ramsay. If the true value is used, a five normal solution of water in acetic acid is more polymerized than is pure water. The conclusions of the authors therefore need revision.  
W. D. B.

**Some physical and chemical properties of strong nitric acid.** *V. H. Velej and J. J. Manley. Jour. Chem. Soc.* 83, 1015 (1903). — "Nitric acid of 96 per-

cent and sulphuric acid of 98 percent concentration show definitely marked characteristics, analogous, although not in all cases strictly parallel, as regards certain properties, more especially density, contraction, and electrical conductivity; also in the case of the former, refractive indices, as investigated by ourselves, and in the case of the latter chemical reactivity, boiling-point, vapor-pressure, and, to a less degree, viscosity and capillarity, as investigated by Knietzsch."

W. D. B.

The state of carbon dioxide in aqueous solution. *J. Walker. Jour. Chem. Soc.* 83, 182 (1903). — The author had previously assumed that Ostwald's dilution law could not hold for carbonic acid if it were assumed that the amount of undissociated carbonic acid was proportional to the unchanged carbon dioxide. Acting on a suggestion by Abegg, he has revised his calculations and finds that the applicability of the dilution law is independent of the degree of hydration.

W. D. B.

#### Multi-Component Systems

Some observations on the system, zinc chloride, ammonium chloride and water. *P. A. Meerburg. Zeit. anorg. Chem.* 37, 199 (1903). — The author has determined the isotherms at 0°, 20° and 30° for the system, zinc chloride, ammonium chloride and water. The only double salts are  $\text{ZnCl}_2 \cdot 2\text{NH}_4\text{Cl}$  and  $\text{ZnCl}_2 \cdot 3\text{NH}_4\text{Cl}$ . This confirms the results of Marignac and of Base. The other six alleged double salts are mythical. The author calls attention to the clearness of Marignac in all this double salt equilibrium. The reviewer is in a position to confirm this with respect to Marignac's work on the double salts of columbium. Marignac's point of view was much more modern than was that of some who followed him.

W. D. B.

On the iodides of caesium. *H. W. Foote. Am. Chem. Jour.* 29, 203 (1903). — A study of caesium iodide, iodine and water, making use of the phase rule. It is shown that  $\text{CsI}_2$  and  $\text{CsI}_3$  are the only addition products existing between -4° and +73°.

W. D. B.

On the thiocyanates of silver and potassium and their solubility. *H. W. Foote. Am. Chem. Jour.* 30, 330 (1903). — At 25° the solid phases in the system potassium sulphocyanate, silver sulphocyanate and water are the two single salts, and two double salts,  $\text{KSCN} \cdot \text{AgSCN}$  and  $2\text{KSCN} \cdot \text{AgSCN}$ . A third double salt,  $3\text{KSCN} \cdot \text{AgSCN}$ , can also be obtained, but is apparently instable at all temperatures.

W. D. B.

On the double caesium and mercuric chlorides and their solubility. *H. W. Foote. Am. Chem. Jour.* 30, 339 (1903). — In the system, caesium chloride, mercuric chloride and water, the solid phases stable at 25° are the two single salts and the double salts  $\text{Cs}_2\text{HgCl}_6$ ,  $\text{Cs}_3\text{HgCl}_4$ ,  $\text{CsHgCl}_3$ ,  $\text{CsHg}_2\text{Cl}_5$ , and  $\text{CsHg}_3\text{Cl}_{11}$ . It is believed that two forms of the compound  $\text{CsHgCl}_3$  can coexist in stable equilibrium with one solution, but this must be an error. The author attempts to show that this is in accordance with the phase rule, but his argument is purely formal and his conclusion is unsound. The fallacy is clear when we apply it to a simpler case, that of sulphur in a mixture of benzene and toluene. According to the author the monoclinic and the rhombic forms might be in equilibrium at 25° in presence of these solvents.

W. D. B.

The lowering of the freezing-point of aqueous hydrogen dioxide by sulphuric and acetic acids. *H. C. Jones and G. Murray. Am. Chem. Jour.* 30, 205 (1903). — When hydrogen dioxide is present in water, the molecular lowerings of the freezing-point on adding sulphuric acid are larger than they would be if no hydrogen dioxide were present. A similar, though less marked phenomenon, was observed when acetic acid was substituted for sulphuric acid. The authors assume that hydrogen dioxide solutions make the acids dissociate more than does water. It is possible that it is really a case of relative solubilities.

W. D. B.

The solubility of ammonia in water containing urea. *F. Goldschmidt. Zeit. anorg. Chem.* 36, 88 (1903). — Urea decreases the solubility of ammonia in water and the author is now convinced that this is not due to a change of dissociation nor to a change of hydration (6, 200); but is merely a plain fact. He thinks that this must be due to both being bases.

W. D. B.

The solubility of ammonia in salt solutions, II. *H. Riesenfeld. Zeit. phys. Chem.* 45, 451 (1903). — From experiments at 25° and 35° it is found that the equivalent relative lowering of the solubility of ammonia is a function of the temperature with  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{NaCl}$  and  $\text{LiCl}$ , while it is not with  $\text{KOH}$ ,  $\text{NaOH}$ ,  $\text{KCl}$ ,  $\text{KNO}_3$ ,  $\text{CH}_3\text{CO}_2\text{K}$  and  $\text{K}_2\text{C}_2\text{O}_4$ . Values of 0.21 for  $\text{NaOH}$  and of 0.26 for  $\text{KOH}$  are interesting instances of the "law" that the lowering of the solubility is independent of the nature of the salt.

W. D. B.

Equilibrium in the system composed of sodium carbonate, sodium bicarbonate, carbon dioxide and water. *H. N. McCoy. Am. Chem. Jour.* 29, 437 (1903). — The author's results are represented by the formula

$$\frac{2x^2C}{kP(1-x)} = K,$$

where " $x$ " is the fraction of the sodium in the form of bicarbonate,  $1-x$  is the fraction in the form of carbonate,  $C$  is the concentration of the sodium in grams per liter,  $k$  is the solubility coefficient of carbon dioxide in water at the equilibrium temperature, and  $P$  is the partial pressure of the carbon dioxide." For dilute solutions  $K = 53 \times 10^3$ . For solutions in equilibrium with air the author finds much less bicarbonate than was found by Cameron and Briggs (5, 537).

W. D. B.

On the evolution of carbon dioxide from sodium carbonate solutions. *F. W. Küster and M. Grütters. Zeit. Elektrochemie*, 9, 679 (1903). — The authors have determined the partial pressure of  $\text{CO}_2$  in equilibrium with different solutions of sodium carbonate, sodium bicarbonate and sodium hydroxide, also the conductivities of these solutions. When these results are plotted against the concentrations, the curves show no signs of breaks at the composition  $\text{Na}_2\text{CO}_3$ . The partial pressures of carbon dioxide were determined by the Ostwald-Walker method and are therefore probably very inaccurate.

W. D. B.

Distillation of chlorine water. *A. Richardson. Jour. Chem. Soc.* 83, 380 (1903). — When chlorine water is distilled, it undergoes partial change with formation of hypochlorous and hydrochloric acids.

"When the separation of the two acids is prevented, chlorine water is practically stable at the boiling-point.

"The amount of change decreases as the distillation proceeds, owing to the formation of hydrochloric acid in the original solution, and in the presence of a large excess of the acid only free chlorine passes over in the distillate."

W. D. B.

**Boric acid, potassium fluoride and hydrofluoric acid.** *R. Abegg, C. J. J. Fox and W. Herz. Zeit. anorg. Chem.* 35, 129 (1903). — When boric acid is added to a solution of potassium fluoride, an alkaline reaction is obtained. The authors have studied this reaction in many ways without coming to an entirely satisfactory conclusion. Potassium fluoride behaves differently from hydrofluoric acid and there appear to be one or more irreversible reactions taking place more or less slowly in the reaction. While  $\text{KBF}_4$  ought to be formed in the potassium fluoride solution, it seems not to be.

W. D. B.

**Reversibility of enzyme or ferment action.** *A. C. Hill. Jour. Chem. Soc.* 83, 578 (1903). — "It is shown that the synthetical action of a maltase-containing yeast-extract on glucose results in the formation of two isomeric bioses — one, not hitherto described, which is now called revertose; the other, although not isolated, is, according to the evidence obtained, in all probability maltose. A small formation of dextrin is attributed to the diastase in the yeast-extract.

"It is shown, further, that both taka-diastase and the pancreatic ferments have a reversible synthetical action on glucose."

From the work that has been done in the last five years the author concludes "that the view he put forward in 1898 is a correct one — namely that all ferment actions are reversible."

W. D. B.

**The classification of the colloids.** *A. Müller. Zeit. anorg. Chem.* 36, 340 (1903). — It is proposed to divide the colloids into two groups. In the first group are to be put the substances which are certainly to be considered in suspension, while the second contains substances of very high molecular weight, such as the albuminoid substances and possibly some of the inorganic sols. In the second group we are dealing with true solubility and therefore with a change of vapor-pressure. Owing to the two high molecular weight the rate of diffusion is low. We have to postulate that these substances have the power when in solution to polarize light. The striking characteristic of this group is that an amorphous precipitate always has a cell structure. The first group is the group to which all colloids belonged before this proposed division and therefore includes all others.

While a classification is eminently desirable, and while there is no reason to doubt the existence of substances with high molecular weights, the assumption that a true solution can polarize light in this way needs confirmation. On the other hand, it seems a good point to separate substances which give a cellular gel from those which do not, though even this distinction will perhaps not stand the test of hostile criticism.

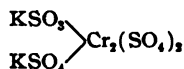
W. D. B.

**On the behavior of the vanadates in aqueous solutions.** *P. Dülberg. Zeit. phys. Chem.* 45, 129 (1903). — The author has studied the change in conduc-

tivity of the vanadates with changing amount of alkali, and has compared these results with the color changes under the same circumstances with different indicators. In addition he has determined molecular weights, transference number and rate of change. The metavanadate has the formula  $\text{Na}_3\text{V}_2\text{O}_6$ ; the ion of the pyrovanadate has the formula  $\text{V}_2\text{O}_7^{4-}$ , while the orthovanadate is decomposed almost completely into pyrovanadate and free caustic. With hydrogen peroxide the vanadium pentoxide can be converted into hexavanadic acid,  $\text{H}_4\text{V}_6\text{O}_{17}$ . In presence of hydroxyl or hydrogen as ion, the ion of hexavanadic acid is decomposed, the reaction being monomolecular. *W. D. B.*

The mechanism of the reduction of potassium dichromate by sulphurous acid. *H. Bassett. Jour. Chem. Soc.* 83, 692 (1903).—“When potassium dichromate, potassium chromate, or chromic acid is reduced by sulphurous acid, 94–95 percent of sulphate is formed together with 5–6 percent of dithionate, the amount of the latter produced being independent of the temperature.

“The freshly reduced solutions do not give the reactions of chromium of  $\text{SO}_4$  ions, and appear to contain a compound



(or the corresponding acid), which slowly decomposes into  $\text{Cr}_2(\text{SO}_4)_3$  and  $\text{K}_2\text{SO}_3$ . If sulphuric acid or potassium sulphate is added to those solutions, the reactions of  $\text{SO}_4$  are not given by the resulting mixture. It seems possible that one molecule of chromium sulphate may mask the reaction of as many as six molecules of sulphuric acid.

“Electrolytic experiments show that the green solutions contain a green anion which decomposes slowly into violet chromium cations and  $\text{SO}_4$  ions.”

*W. D. B.*

The determination of sulphuric acid in presence of zinc. *A. Thiel. Zeit. anorg. Chem.* 36, 84 (1903).—When zinc is present in the solution, too little barium sulphate is precipitated on adding barium chloride. This can be avoided by precipitating the zinc with ammonia before adding the barium chloride and by redissolving the zinc in acid before filtering the barium sulphate.

*W. D. B.*

On the proportion of argon in the vapor rising from liquid air. *Lord Rayleigh. Phil. Mag.* [6] 5, 677 (1903).—The author undertakes a thorough study of the method of preparing argon from the vapor of liquid air. The method proves to be a practical one and useful since the more general introduction of liquid air machines. The proportion of argon is fairly constant and amounts to about 2 percent of the whole. The advantage of starting with liquid air rather than with a mixture of atmospheric air and oxygen of the same proportion is obvious.

*H. T. B.*

Reactions between yellow phosphorus and copper in aqueous solution. *W. Straub. Zeit. anorg. Chem.* 35, 460 (1903).—When a stick of yellow phosphorus is dipped into a copper sulphate solution, it first becomes coated with copper phosphide and then with metallic copper. All the copper is precipitated from the solution and phosphoric acid appears to be formed. About one com-

binizing weight of phosphorus goes into solution for every two of copper precipitated. The author is unable as yet to write an equation for the reaction.

W. D. B.

The theory of the indigo reduction. *A. Binz. Zeit. Elektrochemie*, 9, 599 (1903).—Indigo carmine forms a double compound with alkali. This is advanced as an additional reason why the reduction of indigo by zinc must be a deoxidation. One may agree with the author as to the indigo reduction even if one does not admit the force of this argument.

W. D. B.

The theory of the indigo reduction. *F. Haber. Zeit. Elektrochemie*, 9, 607 (1903).—A reply to Binz (preceding review) in which the interesting argument is put forward that the reduction of indigo by zinc cannot be a direct deoxidation of the metal because other substances reduce indigo.

W. D. B.

### Velocities

Hydrolysis of urea hydrochloride. *J. Walker and J. K. Wood. Jour. Chem. Soc.* 83, 484 (1903).—The hydrolysis of urea hydrochloride was calculated from the rate of inversion of cane sugar, and from the catalysis of methyl acetate. The results are the same in the two cases. Within the range of 25°–40° the temperature has practically no influence on the hydrolysis of urea hydrochloride. The change of hydrolysis with change of concentration is given by the dilution law. The addition of sodium chloride diminishes the degree of hydrolysis very slightly.

W. D. B.

The affinities of some feebly basic substances. *J. K. Wood. Jour. Chem. Soc.* 83, 568 (1903).—The author has determined the percentage hydrolysis in  $n/10$  solutions of the hydrochlorides of urea, thiourea, nitroguanidine, acetoguanidine, biuret, semicarbazide, creatine, creatinine, caffeine, *o*-aminocaffeine, theobromine, guanine, xanthine, acetamide, benzamide, acetanilide, dimethylpyrone and cyneol.

W. D. B.

The rate of inversion of sugar in plastered wines. *G. Magnanini. Zeit. Elektrochemie*, 9, 751 (1903).—When wines have been treated with plaster of Paris, it is usually assumed that acid potassium sulphate is formed. Experiments on the rate at which such a wine inverts sugar show that the neutral salt is formed and not the acid salt.

W. D. B.

The hydrolysis of organic peroxides and peracids. *A. M. Clover and G. F. Richmond. Am. Chem. Jour.* 29, 179 (1903).—Propionic peroxide in aqueous solution is gradually changed to propionic peracid and propionic acid.



The rate of change is approximately what it should be for a monomolecular reaction.

W. D. B.

The decomposition of carbon monoxide. *R. Schenck. Zeit. Elektrochemie*, 9, 691 (1903).—A study of the rate of decomposition of carbon monoxide in presence of nickel, iron and other metals. The reaction is apparently of the first order at the lower temperatures and bimolecular at the higher. This may be due to the reaction not taking place at constant temperature.

W. D. B.

**On the first anhydrous form of gypsum.** *P. Rohland. Zeit. anorg. Chem.* 36, 332 (1903). — Ammonium, magnesium and calcium chlorides retard the hydration of the first anhydrous form of calcium sulphate, although the first two accelerate the hydration of the hemihydrate. Since the anhydride can become hydrated by long standing, by contact with positive catalyzers, or after having been heated to 525°, the author inclines to the view that hydration is a process taking place spontaneously but at different rates under different conditions.

W. D. B.

**The rusting of iron and the passive state.** *M. Mugdan. Zeit. Elektrochemie*, 9, 442 (1903). — The author finds that the rate of oxidation of iron by air varies with the nature of the salt in solution. The solution is believed in some cases to have a catalytic action on the iron, making it passive. It is interesting to note that iron will not precipitate copper from an acetate solution. If a little sodium chloride be added, however, the copper is precipitated.

W. D. B.

**On the rates of reaction in reductions.** *H. Goldschmidt. Zeit. Elektrochemie*, 9, 725 (1903). — When nitro compounds are reduced by hydrogen sulphide in presence of sulphhydrates, the rate is proportional to the concentrations of the nitro compound and the sulphhydrate as ion, and practically independent of the concentration of the hydrogen sulphide. In the reduction by stannous chloride in acid solution, the rate of reaction is proportional to the concentrations of the nitro compound, the stannous chloride and the hydrochloric acid. From this it follows that tin as ion cannot be one of the active substances. The reaction passes through the nitroso stage. Special experiments showed that nitroso benzene and stannous chloride react instantaneously.

W. D. B.

**The slow oxidation of methane at low temperatures, II.** *W. A. Bone and R. V. Wheeler. Jour. Chem. Soc.* 83, 1074 (1903). — Experiments on a larger scale and with a modified apparatus have enabled the author to detect the intermediate formation of formaldehyde and formic acid when methane and oxygen are heated to 300°–400°.

W. D. B.

**The mechanism of combustion.** *H. E. Armstrong. Jour. Chem. Soc.* 83, 1088 (1903). — The author postulates that it is necessary to regard all phenomena from one point of view and to assume that chemical interchange and electrolysis are interchangeable equivalent terms. He then discusses the general problem of oxidation with special reference to the work of Dixon, attacking the interpretation offered by the latter.

W. D. B.

#### *Electromotive Forces*

**The absolute potential of the calomel electrode.** *W. Palmaer. Zeit. Elektrochemie*, 9, 754 (1903). — In potassium cyanide and hydrogen sulphide solutions, mercury can be made to change the sign of the electrical charge. The author has determined, by means of the flowing electrode, the concentrations at which this takes place. From this he deduces a potential difference of 0.57 volt for the calomel electrode.

W. D. B.

On the reproducibility of the electromotive forces of some strong oxidizing agents. *J. Scobai. Zeit. Elektrochemie*, 9, 879 (1903).—When potassium permanganate, manganese peroxide, chromic oxide or sodium persulphate is mixed with  $n$ ,  $12n$ ,  $22n$ , or concentrated sulphuric acid, the potential of a platinum plate in one of these mixtures has a very definite value. With manganese dioxide, the constant potential was reached quickly, while a relatively long time was necessary with potassium permanganate or chromic oxide.

W. D. B.

The electromotive behavior of the oxides of cerium. *E. Baur and A. Glaessner. Zeit. Elektrochemie*, 9, 534 (1903).—Measurements of electromotive force were made with cerous and ceric sulphate solutions; with cerous and ceric nitrate solutions; with alkaline cerous and ceric nitrate solutions; with alkaline ceric and cerium peroxide solutions. The changes of the potential with the concentration could not be expressed by a formula. Some experiments were made with alkaline ceric solutions and reducing agents.

W. D. B.

Berthelot's law relative to the electromotive forces of cells based on the reciprocal action of saline solutions and soluble electrolytes. *C. J. Reed. Trans. Am. Electrochem. Soc.* 4, 151 (1903).—Berthelot has put forward the following generalization: "When a base acts upon an acid, the electromotive force developed is the sum of the electromotive forces developed by the reaction of the corresponding salt separately upon the acid and upon the base. The reacting solutions are supposed to be dilute, in equivalent proportions, and to give rise to no separation of gaseous or insoluble products and to undergo no progressive change in their internal constitution other than neutralization".

For this statement the author proposes to substitute the following:—"When a base acts upon an acid, the electromotive force developed is zero. When a salt acts upon the corresponding acid or the corresponding base, the electromotive force developed is also zero. The electromotive force at the junction of two electrolytes, whether chemical reaction takes place or not, is zero under all circumstances. The electromotive force between a platinum plate and an acid, and the electromotive force between a platinum plate and a base measured separately, equals the sum of these electromotive forces measured simultaneously."

W. D. B.

Contribution to the electrolysis of aqueous solutions. *C. Frenzel. Zeit. Elektrochemie*, 9, 487 (1903).—When ammonia is electrolyzed between platinum electrodes with ever-increasing potential difference, the anode potential shows the existence of a premature break which appears to be due to the presence of oxygen dissolved in the anode. This is discussed with reference to Luther's experiments on ozone.

W. D. B.

The electrolysis of water, II. *J. W. Richards and E. S. Landis. Trans. Am. Electrochem. Soc.* 4, 111 (1903).—The authors have made measurements on the difference of potential between the ends of capillary tubes and of the current flowing as a result of this potential difference. There is nothing in the paper to show whether the resistance of the voltmeter was or was not taken into account. If this were not done, the potential differences actually



given probably differ greatly from the real potential differences. Since the authors do not distinguish between "decomposition voltages" and the difference of potential between the electrodes, they speak of the decomposition voltage as being higher than 110 volts under certain circumstances.

On the other hand they record the interesting statement that visible evolution of gas takes place only when the current density at either or both of the electrodes becomes equal to five microamperes per square meter. Even here we are left in doubt whether this value may not be a function of the shape of the vessel and of the time.

W. D. B.

On the stability of salts with oxidizable cations and anions. *R. Abegg. Zeit. Elektrochemie*, 9, 569 (1903). — A discussion of the stability of certain salts based on the consideration that the sum of the anode and cathode potentials cannot be positive.

W. D. B.

On "insoluble" anodes especially in the electrolysis of hydrochloric acid. *R. Luther and F. J. Brislée. Zeit. phys. Chem.* 45, 216 (1903). — At smooth platinum anodes, the reversible evolution of chlorine is a secondary process and depends on the state of the anode, it being necessary to assume three modifications of the platinum surface. These three have been studied in their relations one to the other. With iridium anodes, a material was found which behaved like platinized platinum but which did not become passive.

W. D. B.

On the specific electrical resistance of non-metallic conductors of the first class. *P. Ferchland. Zeit. phys. Chem.* 9, 670 (1903). — The author finds a specific resistance of 0.003–4 ohms for a centimeter cube of lead peroxide. This is about fifteen times as large as that found by Streintz, and the author attributes the discrepancy to varying amounts of water in the lead peroxide.

W. D. B.

#### *Electrolysis and Electrolytic Dissociation*

The quantitative electrolytic precipitation of metals. *P. Denso. Zeit. Elektrochemie*, 9, 463 (1903). — The author advocates precipitating copper by Freudenberg's method of constant potential, using a single storage cell. Stirring the solution increases the rate of precipitation. Platinizing the anode is also useful. Cadmium can be precipitated in an acid solution, using a higher voltage than is necessary for copper, while zinc does not precipitate.

W. D. B.

Quantitative electrolytic determination of thallium as oxide at the anode. *M. E. Heiberg. Zeit. anorg. Chem.* 35, 347 (1903). — If acetone is added to an acid solution of thallium sulphate, the oxide  $Tl_2O_3$  can be precipitated quantitatively in a good weighable form at the anode with a low current density and a temperature of 50°–55°. At first some metallic thallium precipitates at the cathode, but this redissolves. If the solution is made so acid that no thallium is set free at the cathode, it is difficult to precipitate all the oxide.

W. D. B.

The electrolytic estimation of minute quantities of arsenic, more especially in brewing materials. *T. E. Thorpe. Jour. Chem. Soc.* 83, 969 (1903). — A description of the method in use at the Government Laboratory in London of determining arsenic electrolytically.

W. D. B.

**Galvanotechnique and photography.** *J. Rieder. Zeit. Elektrochemie*, 9, 911 (1903). — A description of some experiments on precipitating thin films of lead peroxide anodically on a daguerreotype plate. While this gave colored pictures, they were not true to life. The article is published in order to draw attention to the subject. *W. D. B.*

**On plumbic salts.** *K. Elbs and R. Nübling. Zeit. Elektrochemie*, 9, 776 (1903). — The authors describe the conditions necessary for preparing plumbic chloride, plumbic pyrochromate and plumbic phosphate. With hydrobromic, hydriodic and fluosilicic acids, no plumbic salts could be obtained. *W. D. B.*

**A contribution to the preparation of nitrite by electrolytic reduction of aqueous nitrate solutions.** *E. Müller and J. Weber. Zeit. Elektrochemie*, 9, 955 (1903). — By working in a slightly alkaline nitrate solution with a spongy copper cathode, it was possible to obtain 93 percent reduction to nitrite with only an 0.7 percent reduction to ammonia. It is necessary to depolarize the cathode occasionally by making it anode for a moment. Platinum cannot be substituted for copper. The authors believe that in this case they are dealing with a specific chemical action of the copper. This is practically the theory of Bintlz. A number of measurements were made of the potential differences at the cathode. These showed that nitrate is more readily reduced than nitrite when copper cathodes are used, while the reverse is the case with platinum cathodes. *W. D. B.*

**The electrolytic reduction of *p*-nitrotoluene in hydrochloric acid solution in presence of formaldehyde.** *E. Goetze. Zeit. Elektrochemie*, 9, 470 (1903). — The author repeated Löb's experiments on the reduction of *p*-nitrotoluene in order to establish the fact that the base thus obtained was identical with one prepared chemically by Troeger. This proved to be the case and the substance is trimethylene tritoluidine. *W. D. B.*

**The electrolytic reduction of phenomorpholones and naphthomorpholones.** *T. H. Lees and F. Shedden. Jour. Chem. Soc.* 83, 750 (1903). — The reductions were made in sulphuric acid solutions with lead electrodes as prescribed by Tafel. Even at temperatures below 30° the reduction products of phenomorpholone were acetyl-*o*-aminophenol, ethyl-*o*-aminophenol and isoacetyl-*o*-aminophenol, but no phenomorpholine. The reduction products of *N*-methyl phenomorpholone were *N*-acetylmethyl-*o*-aminophenol, *N*-methylethyl-*o*-aminophenol, and *N*-methyl phenomorpholine. The reduction product of *N*-methyl- $\beta$ -naphthomorpholone was chiefly *N*-methylethyl- $\alpha$ -amino- $\beta$ -naphthol, though *N*-methyl- $\beta$ -naphthomorpholine was also formed in small amount. *W. D. B.*

**On the electrolytic reduction of unsaturated compounds.** *C. Marié. Zeit. Elektrochemie*, 9, 633 (1903). — Using a mercury cathode in an alkaline solution, there is no difficulty in reducing such substances as fumaric and cinnamic acids to the saturated compounds. *W. D. B.*

**Process for electrolytic preparation of vanadium and its alloys.** *G. Gin. Zeit. Elektrochemie*, 9, 831 (1903). — The anodes are made of vanadium trioxide and carbon, the cathode is steel, and the bath is iron fluoride dissolved in

calcium fluoride. A more close approximation to the aluminum process would probably yield better results. W. D. B.

**Note on the electrometallurgy of gold.** *W. H. Walker. Trans. Am. Electrochem. Soc.* 4, 47 (1903).—After a brief sketch of the Siemens and Halske, Pelatan-Clerici, and Aurex sluice processes for extracting gold, the author describes some experiments of his own with gold telluride. When gold telluride is laid on a platinum cathode in an alkaline solution, metallic gold is deposited on the platinum and tellurium is set free. W. D. B.

**On decompositions in potassium silver cyanide baths.** *E. Jordis and W. Stramer. Zeit. Elektrochemie*, 9, 572 (1903).—The decomposition of cyanide in a silver-plating bath takes place more rapidly when the current is flowing than when the bath is resting. While much of the anode decomposition is due to the formation of carbonate, other substances are also formed. The statement in the books that new silver baths do not work well is said by the authors to be incorrect. W. D. B.

**The voltametric balance.** *W. Pfanhauser. Zeit. Elektrochemie*, 9, 668 (1903).—A description of an instrument devised by the author for breaking the circuit when substances have been plated to the proper weight with silver. There seems to be a tacit assumption that the current efficiency is practically one hundred percent in a silver-plating bath. W. D. B.

**Note on disturbance with lead anodes in soda solutions.** *K. Elbs and E. Stohr. Zeit. Elektrochemie*, 9, 531 (1903).—In the electrolytic reduction of nitro compounds, it is often desirable to use a lead anode in a soda solution. If the soda solution contains chloride, there is formed on the anode a thick crust of peroxide, chloride, and hydroxide, which increases the resistance very much. An impurity of sulphate is not serious. W. D. B.

**A suggested theory of the aluminum anode.** *W. W. Taylor and J. K. H. Inglis. Phil. Mag.* [6] 5, 301 (1903).—The essential peculiarities of an aluminum anode are reproduced by means of a platinum anode and a film of aluminum hydroxide. The influence of chloride, bromide, nitrate, acetate, chlorate, and thiocyanate on an aluminum anode in sulphuric acid was investigated. The authors believe that the film is to be regarded as a membrane permeable to some ions and impermeable to others. H. T. B.

**Electrolysis of sodium hydroxide by alternating current.** *C. Hambuechen. Trans. Am. Electrochem. Soc.* 4, 105 (1903).—Caustic soda was fused in an aluminum vessel and electrolyzed with an alternating current, using an iron and an aluminum electrode separated by an aluminum diaphragm. Sodium was obtained without difficulty, and the corrosion of the aluminum electrode was only about 0.5 gram for fifty ampere-hours. W. D. B.

**Pyrogenic reactions and syntheses by means of the electric current, III.** *W. Löb. Zeit. Elektrochemie*, 9, 903 (1903).—The author has studied the effect of an electrically heated wire on benzyl chloride, on benzal chloride and benzo trichloride. With the first, stilbene was the chief product, though traces of phenanthrene were observed. With the second, the chief product is

a mixture of the two toluene dichlorides. With the third, the chief product is toluene trichloride, identical with Blank's ditoluene hexachloride. *W. D. B.*

The measurement of ionic velocities in aqueous solution, and the existence of complex ions. *B. D. Steele. Phil. Trans. 198A, 105 (1902).*—Reviewed (6, 444) from *Jour. Chem. Soc.* 79, 414 (1901); *Zeit. phys. Chem.* 40, 689 (1902).

An experiment on the electrolytic determination of the basicity of acids. *I. J. Moltkehanzen. Trans. Am. Electrochem. Soc.* 4, 39 (1903).—When cupric chloride is heated with orthophosphoric acid, copper metaphosphate is formed. Ammonium metaphosphate,  $(\text{NH}_4\text{PO}_3)_2 \cdot 2\text{H}_2\text{O}$ , is obtained by treating copper metaphosphate with ammonium sulphide. From the change of conductivity of ammonium metaphosphate with changing concentration, the author concludes that the salt is a dimetaphosphate. *W. D. B.*

On the determination of the neutralization point by conductivity measurements. *F. W. Küster and M. Grütters. Zeit. anorg. Chem.* 35, 454 (1903).—By measuring the conductivity it is easy to determine the end-point and this method is recommended whenever the color or the formation of a precipitate prevents the use of an indicator [effect of temperature changes?]. For accurate measurements with phenol phthaleine as indicator, barium hydroxide should always be used instead of sodium or potassium hydroxide. Readings with methyl orange depend upon the volume and the concentration of neutral salts. *W. D. B.*

The relative affinities of polybasic acids. *H. M. Dawson. Jour. Chem. Soc.* 83, 725 (1903).—It is pointed out that the distribution of a base between a monobasic acid like hydrochloric acid and a strong dibasic acid like sulphuric acid cannot be strictly proportional to the relative concentrations of hydrogen as ion because we are really dealing with three acid radicals,  $\text{Cl}'$ ,  $\text{HSO}'_4$ , and  $\text{SO}'_4$ , instead of two. *W. D. B.*

Note on metallic diaphragms. *E. A. Byrnes. Trans. Am. Electrochem. Soc.* 4, 135 (1903).—Crushed magnetite is said to form an excellent diaphragm for use in fused sodium hydroxide. *W. D. B.*

#### Dielectricity and Optics

The action of ozone, hydrogen peroxide, etc., on carbon monoxide. *W. A. Jones. Am. Chem. Jour.* 30, 40 (1903).—When air and carbon monoxide are passed over moist phosphorus small quantities of carbon dioxide are formed. Carbon monoxide is not oxidized appreciably by phosphorus and hydrogen peroxide. Using a Berthelot ozonizer with six bichromate cells connected with the coil, carbon monoxide was oxidized at ordinary temperatures and still more at 250°. With only two cells carbon dioxide was formed at 250°, but not at ordinary temperatures. The effect of the ozone therefore depends on concentration and temperature. Neither concentrated hydrogen peroxide nor electrolytic oxygen oxidizes carbon monoxide. *W. D. B.*

The action of ozone on carbon monoxide. *C. E. Waters. Am. Chem. Jour.* 30, 50 (1903).—These experiments differ from those of Jones (preceding

review) in that a Holtz machine was used with the Berthelot ozonizer instead of an induction coil. In dry weather this made little difference; but in damp weather very little ozone was formed. Even at best there is very little oxidation at ordinary temperatures. *W. D. B.*

The absorption spectra of nitric acid in various states of concentration. *W. N. Hartley. Jour. Chem. Soc. 83, 658 (1903).* — When a nitric acid of sp. gr. 1.490 is diluted the spectrum is lengthened. With acids of sp. gr. 1.432 down to 1.127, dilution decreases the length of the spectrum. The author believes that this is due to the existence in solution of hydrates of nitric acid.

*W. D. B.*

A method for determining the index of refraction of solid hydrocarbons with the Pulfrich refractometer. *C. F. Mabery and L. Shepherd. Am. Chem. Jour. 29, 274 (1903).* — The authors do not really measure the refractive index of the solids at all; they measure solutions and calculate the value of the solid assuming the law of mixtures. The solutions in the cup of the refractometer are kept heated by an electric current passing through a coil of wire. *W. D. B.*

The influence of molybdenum and tungsten trioxides on the specific rotations of *l*-lactic acid and potassium *l*-lactate. *G. G. Henderson and J. Prentice. Jour. Chem. Soc. 83, 259 (1903).* — The addition of molybdenum or tungsten trioxide to an aqueous solution of potassium *l*-lactate causes an increase in the rotation which reaches a maximum when there is one molecular weight of the oxide to two of the lactate. Tungsten trioxide is practically insoluble in a solution of *l*-lactic acid, but molybdenum trioxide dissolves, the maximum rotation being reached when there is one molecular weight of the oxide to one of the acid as against two of the lactate. *W. D. B.*

The combination of carbon monoxide with chlorine under the influence of light. *G. Dyson and A. Harden. Jour. Chem. Soc. 83, 201 (1903).* — When a mixture of carbon monoxide with chlorine, dried by being passed through sulphuric acid, is exposed to light, a well-marked period of photochemical induction occurs. The effect of induction disappears slowly when the exposed gas is placed in the dark. The period of photochemical induction is greatly diminished by an admixture of air, but does not appear to be specifically affected by the presence of carbonyl chloride, hydrogen chloride, excess of carbon monoxide, carbon tetrachloride vapor, and small amounts of water vapor.

*W. D. B.*

#### *Crystallography, Capillarity and Viscosity*

Crystallized ammonium sulphate and the position of ammonium in the alkali series. *A. E. H. Tutton. Jour. Chem. Soc. 83, 1049 (1903).* — Ammonium sulphate stands in the series of normal alkali sulphates between rubidium and caesium sulphates and very close to the rubidium salt when we consider the following properties: "solubility in water, molecular volume, the average distances apart of contiguous molecules along the three axial directions, the refractive indices, the axial ratios of the optical ellipsoid, the directional molecular refraction, the mean refraction equivalent for the crystals, the refractive

equivalent for the state of solution in water, and the general optical scheme which governs the optic axial angle phenomena". *W. D. B.*

The fracture of metals under repeated alternations of stress. *J. A. Ewing and J. C. W. Humfrey. Phil. Trans. 200A, 241 (1903).* — The metal chosen for experiment was Swedish iron having a tensile strength of 23.6 tons/sq. inch and showing a proportionality of strain to stress up to 12 or 13 tons per square inch with no apparent defect of elasticity. When subjected to repeated reversals of a stress of 5 tons per square inch, no damage could be detected. With 7 tons signs of fatigue were noticed, though no cracks were formed within the limits of the experiments. With 9 tons the metal broke. This breaking is due to the appearance of slip-bands which finally develop into cracks. The more frequent the reversals, the lower the breaking stress. Rest or heating to 100° causes a gradual healing. *W. D. B.*

Surface tension of polarized mercury. *G. Kucera. Drude's Ann. 11, 529, 698 (1903).* — According to the theory of capillarity, the surface tension,  $a_{12}$ , at the boundary between two liquids of surface tension  $a_1$  and  $a_2$ , respectively, is given by the relation :

$$a_{12} = a_1 + a_2 - 2A_{12},$$

where  $A_{12}$  is taken to be the adhesion or molecular attraction between the two liquids. The object of the present work is to determine the dependence of the adhesion on the concentration of the solution for polarized mercury surfaces in different liquids. A dropping method was used for the determination of the surface tension of the polarized surface for which a theory is developed.

Electrocapillary curves are given, and the value of the E. M. F. for the maximum surface tension of a number of solutions is given. Some light is thrown on the action of the capillary electrometer. *H. T. B.*

On the thickness of the liquid film formed by condensation at the surface of a solid. *A. J. Parks. Phil. Mag. [6], 5, 517 (1903).* — By weighing the film of moisture deposited on a glass surface of known area the author finds that the thickness of the film varies between  $10 \times 10^{-6}$  and  $80 \times 10^{-6}$ . The water film on glass in saturated vapor at 15° C is about  $13.4 \times 10^{-6}$  cm in thickness. *H. T. B.*

On the cleansing power of soap. *H. W. Hillyer. Jour. Am. Chem. Soc. 25, 511 (1903).* — "The cleansing power of soap is largely or entirely to be explained by the power which it has of emulsifying oily substances; of wetting and penetrating into oily textures; and of lubricating texture and impurities so that they may be removed easily. It is thought that all of these properties may be explained by taking into account the low cohesion of the soap solutions and their strong attraction, adhesion, or affinity to oily matter, which together cause the low surface-tension between soap solution and oil." *W. D. B.*

Precipitation membranes or cells in gels or solutions of lime, albumen and starch. *G. Quincke. Drude's Ann. 11, 449 (1903).* — The author continues his work on cell and fluid precipitate formation resulting from the surface tension at the boundary between inorganic and organic colloids. *H. T. B.*

The surface tension at the boundary of aqueous colloid solutions of different concentration. *G. Quincke. Drude's Ann.* 10, 478, 673 (1903). — Organic colloids form the subject of a paper of seventy-three pages, which is but a continuation of the work, that has already run through six numbers and embraced 294 pages. Such a complete and exhaustive research should leave little to be found out in regard to colloidal solutions. Size, albumen, tannin, starch tragant and agar are the colloids employed, and like the inorganic colloids they form with water two solutions A and B, one with much and the other with little water, giving rise to a surface tension on the common boundary. In general, it is shown that inorganic and organic colloids show similar phenomena, and differ in properties quantitatively rather than qualitatively.

Illustrations are given of the various forms produced at the boundary surface of solutions A and B, owing to the strong surface tension. The character of the solutions is studied at length, giving rise to a large number of interesting facts.

H. T. B.

Surface tension and cell formation of tannate of glue solutions. *G. Quincke. Drude's Ann.* 21, 54 (1903). — The author continues his work on organic colloids. See previous reviews.

H. T. B.

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==THE==  
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# DECOMPOSITION CURVES OF LITHIUM CHLORIDE IN ALCOHOLS, AND THE ELECTRODEPOSITION OF LITHIUM<sup>1, 2</sup>

BY HARRISON EASTMAN PATTEN AND WILLIAM ROY MOTT

*Introduction.* — Decomposition curves of lithium chloride have been determined, using as solvent several members of the carbinol series, water being taken as the first member. Lithium was deposited from ethyl,<sup>3</sup> propyl, butyl, and amyl alcohols. In addition, solutions of lithium chloride in allyl alcohol, in phenol, and in glycerine were tried.

*Materials.* — The solvents used were from Kahlbaum. The lithium chloride was made by E. de Haën.

*Method and Apparatus.* — The solutions were electrolyzed in a glass cell with fused-in platinum electrodes, 1.2 cm wide by a little less than 2.5 cm long and placed about 7 mm apart. The cell was fitted with a ground-in glass stopper which served to exclude the moisture of the air. A continuous variation in

<sup>1</sup> An abstract of this paper has appeared in the *Electrochemical Industry*, Vol. I, No. 12, under the title "Deposition of Lithium from Various Alcohols." This article was sent to the Secretary of the American Chemical Society to be read at the meeting held June 29, 1903. Owing to lack of time, it was not included in the program. The abstract was given to Dr. Roeber for publication to secure proper credit for the work.

<sup>2</sup> We reserve all patent rights. Our claims, stated broadly, are as follows: We have discovered and used new classes of solvents for the electrolytic separation of alkali metals (such as lithium, sodium, etc.) and alkaline earth metals (such as magnesium, calcium, strontium, etc.), and other metals not easily obtained from aqueous solutions. We define and claim as our invention, the use of organic solvents fulfilling the two conditions: First, there should be present in the solvent not less than three carbon atoms. Second, one or more of these carbon atoms should (*a*) be the center of a carbonyl group [which includes ketones (such as acetone, etc.) and aldehydes] or (*b*) have bound to it an hydroxyl group (this includes propyl alcohol, butyl alcohol, amyl alcohol, phenol, etc., etc.).

<sup>3</sup> Lithium was first obtained in this laboratory from ethyl alcohol by Mr. J. G. Zimmerman upon a rotating cathode, using a high current density. This work was done independently of us and was brought to our notice after we had done our work upon the ethyl alcohol solution.



the E. M. F. applied to the cell, was affected by a shunt from a water rheostat. Small currents were measured by taking with a null method the fall of potential across a known resistance and then computing the current according to Ohm's law. Larger currents were read on a milli-ampere meter or on an ammeter. For several solutions anode and cathode curves were taken by inserting a normal electrode,<sup>1</sup> whose voltage was taken as  $-0.56$  volt. Further details are given in a previous paper,<sup>2</sup> which deals in part with the determination of current — E. M. F. curves. In this paper, in reference to the method of measuring small residual currents, it was stated that one of us<sup>3</sup> would soon publish "the details of this method and some of its applications." Instead it is described below.<sup>4</sup>

This method of measuring small currents has not, to our knowledge, been applied to the study of decomposition curves. The methods described by Carhart and Patterson<sup>5</sup> are not convenient for measuring *quickly* currents of wide ranges of strength.

Figure 1 shows the electrical connections used in determin-

<sup>1</sup> Ostwald. *Physiko Chemische Messungen*, p. 258. Also H. R. Carveth. *Jour. Phys. Chem.* 2, 289 (1898).

<sup>2</sup> *Trans. Am. Electrochem. Soc.* 3, 317 (1903).

<sup>3</sup> W. R. Mott.

<sup>4</sup> Accurate measurements of currents much less than one milli-ampere are not only desirable but quite necessary for a thorough study of decomposition curves. Particularly is this true for non-aqueous solutions which in general exhibit higher resistance than aqueous solutions. This method may serve for : (1) Study of total residual current for different electrolytes and different electrodes. (2) Determination of small currents between two mercury surfaces in connection with the Lippmann electrometer and the phenomenon of electrocapillarity in general. (3) For cells such as those containing aluminum electrodes and exhibiting a rectifying effect upon the alternating current. (4) For cells containing high resistance diaphragms, and as an extension of this we may determine the current flowing in organic tissue, either living or dead — a well recognized method of discriminating between live and dead matter. In this connection may be studied, too, the physiological effect corresponding to different *current densities* of wide range. A possible use may be found in determining the relation between muscular contraction and electrical stimulus. (5) The accurate measurement of very large resistances is also readily made. For example, non-aqueous electrolytes, oils, insulators, graphite resistances, metallic films, etc.

<sup>5</sup> Carhart and Patterson. *Electrical Measurements*, pp. 170-172.

ing the current E. M. F. curves across the total cell. A set of storage batteries or a direct current dynamo is connected across AB, which offers a suitable fall of potential. Bose,<sup>1</sup> Lorenz,<sup>2</sup> and others use a wire for the resistance, AB. In this research we substituted a water rheostat, consisting of copper electrodes dipping into aqueous copper sulphate in a paraffined wooden trough, four feet long, four inches deep and three inches wide — internal measurements. A third copper electrode, K, immersed in the electrolyte, served in place of the usual sliding contact. The current passing through the electrolytic cell, C, was measured by the ammeter, A, or by a milli-ammeter. For small currents,

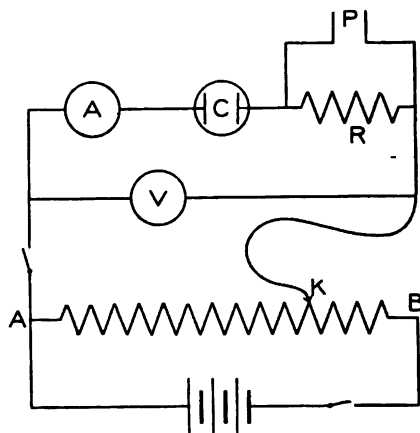


Fig. 1

the zero method previously referred to was used. That is, the current passes through the known wire resistance, R, and the consequent CR drop is measured by a potentiometer apparatus<sup>3</sup> connected to the leads at P. The use of the *variable* resistance, R, to measure the current is somewhat similar to the use of a fixed resistance of 0.1 ohm which Lorenz<sup>4</sup> recommends for decomposition curve determinations. The resistance, R, should

<sup>1</sup> Emil Bose. Zeit. Electrochemie, p. 153 (1898).

<sup>2</sup> Richard Lorenz. Electrochemical Practice, p. 196 (1901).

<sup>3</sup> This potentiometer apparatus is made after a design by Prof. C. F. Burgess. See Carl Hambuechen, Bull. Univ. Wis. No. 42, Eng. Series, p. 246.

<sup>4</sup> Richard Lorenz. Electrochemical Practice, p. 196 (1901).

be capable of ready variation from 100,000 to 10 ohms. (The usual 10,000 ohm resistance box serves most purposes.) The voltmeter, V, measures the total volts across the cell, C, and across the resistance, R. The volts across R are given direct on the potentiometer. By subtracting this voltage on R from the voltmeter reading we get then, the volts applied to the cell. For more accurate measurements of the volts on the cell, C, leads are taken from its terminals to the potentiometer at P and the E. M. F. determined exactly as for the CR drop across R.

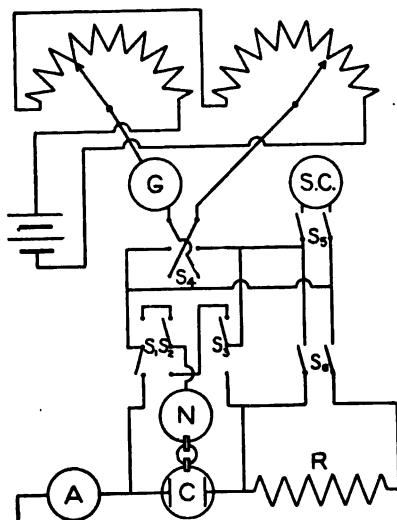


Fig. 2

Fig. 2 represents a more complete and convenient arrangement of connections which we used in determining anode and cathode E. M. F. current curves, discharge potentials, single potentials, and the voltage applied to the cell, C, (more accurately than could be read on the voltmeter). As in Fig. 1, A is the ammeter, C the cell containing the electrolyte to be studied, and R the known resistance across which the CR drop is measured by running leads to the potentiometer. This is effected by closing the switch S<sub>6</sub>, while the switches S<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub> and S<sub>5</sub> are open, and throwing the reversing switch S<sub>4</sub> in the proper direction. The cells at the left which furnish E. M. F. across the total wire of

the potentiometer are checked from time to time by comparison with a standard Weston cell,<sup>1</sup> S. C., which is let into the galvanometer<sup>2</sup> (G) circuit on closing the switch, S<sub>5</sub>. During this reading the switches, S<sub>6</sub>, S<sub>3</sub>, S<sub>2</sub>, S<sub>1</sub>, are of course open. These switches, S<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub>, together with the normal electrode, N, which connects with the cell, C, by a siphon through an intermediate vessel,<sup>3</sup> containing normal potassium chloride, serve to determine total and single difference of potential for the cell, C. Inspection of Fig. 2 will show the necessary adjustment of the switches. The E. M. F. applied to the cell, C, is furnished as in Fig. 1 by a storage battery, and the E. M. F. actually used controlled by the water rheostat mentioned above.

In practice the adjustment of R is important; it is found advisable to calculate the values of R to be used as more and more E. M. F. is applied to C. Otherwise it is possible to retrace part of the current — E. M. F. curve instead of going on up the curve as one desires. Much time may be saved also by adjusting R so that the increment of volts is constant. Owing to the large CR effect of, for example, 10,000 ohms in absorbing E. M. F. applied to the cell, the actual increment of volts on the cell may be very small, while the increment as read on the voltmeter may be large.

The voltage on R should not exceed the safe voltage for which the box is built. Usually this limit is near two volts.

#### Solubility of lithium chloride in alcohols

In depositing alkali metals electrolytically, saturated solutions are most desirable. Lithium chloride was fused, allowed to solidify, broken up while still hot and added to the solvent, which was then heated and shaken some time with excess of the solid salt. For rigid work one needs the exact temperature for which the solubility is taken.<sup>4</sup> However it was not our aim to

<sup>1</sup> Set up, tested, and kindly loaned to us by Mr. F. L. Shinn.

<sup>2</sup> A switch not given in Fig. 2 serves to throw the galvanometer (G) in quickly.

<sup>3</sup> A second intermediate vessel filled with the same solution as in cell C, was frequently found necessary to insure a very slow diffusion of moisture.

<sup>4</sup> The solubility of LiCl in water increases 0.8 percent per 1° C.

prepare saturated solutions under a set of constant conditions, but rather to secure reproducible working conditions. Table I gives the solubility of lithium chloride in several alcohols expressed in percent by weight on the total weight of solution at  $25^{\circ}\text{C} \pm 0.03^{\circ}$ . Water is included as being the first member of the carbinol series; its solubility at  $25^{\circ}\text{C}$  was calculated by interpolation from the data given in Comey.<sup>1</sup>

TABLE I.  
Solubility of LiCl in Alcohols

Solvent	Percent
Water	45.0
Ethyl alcohol	2.475
Propyl alcohol	3.720
Butyl alcohol	9.56
Amyl alcohol	8.26
Allyl alcohol	4.20
Glycerine	4.14
Phenol <sup>2</sup>	1.89

The values in Table I were obtained by diluting with water a weighed portion of the solution, precipitating the chlorine as silver chloride and weighing in the usual manner.<sup>3</sup>

According to Schlamp<sup>4</sup> propyl alcohol dissolves 15.86 parts of lithium chloride per 100 parts of the alcohol. We infer the solubility was for a higher temperature. We have found no references to the solubility of lithium chloride in butyl alcohol as yet. The high value given in Table I is of interest in connection with the low current density at which lithium was deposited from this solvent. Excepting water, butyl alcohol dissolves more lithium than any solvent we have tried. As a mean of five determinations, Andrew and Ende<sup>5</sup> give 6.47 percent as the solubility of lithium chloride in isoamyl alcohol. Gooch<sup>6</sup> gives data

<sup>1</sup> Dictionary of Chemical Solubilities.

<sup>2</sup> Near the melting-point of the solution, at  $53^{\circ}\text{C}$ .

<sup>3</sup> For exact method used, see Chromic Hydroxide in Precipitation. *Am. Chem. Jour.* 18 (1896).

<sup>4</sup> *Zeit. phys. Chem.* 14, 272 (1894).

<sup>5</sup> *Ibid.* 17, 136 (1895).

<sup>6</sup> *Fres. Zeit.* 26, 356.

which indicate 7.8 percent as the solubility. The rate at which the salt dissolves has to do with this discrepancy. Heating the solvent in contact with the compact fragments of anhydrous lithium chloride and shaking vigorously will not saturate the solvent. In one case a continued increase in the quantity dissolved was observed. After a week, 3.63 percent lithium chloride had dissolved at 22° C — less than half of that given in Table I. The solutions we used for electrolyzing stood some two months in contact with excess of salt, so it seems reasonable to assume that equilibrium had been reached. In fusing the lithium chloride, some oxide was formed; but this is insoluble in amyl, propyl, and butyl alcohol and acetone. Their solutions when diluted by water gave no alkaline reaction with either litmus or phenolphthalein.

#### Polarization voltages and the deposition of metallic lithium

The validity of Faraday's law has been tested by Kahlenberg,<sup>1</sup> and salts dissolved in pyridine have been electrolyzed by Laszczynski and Gorski,<sup>2</sup> who appear to have been the first to deposit an alkali metal from solution in the metallic state and unalloyed. Their use of a diaphragm made necessary a pressure of 100 volts to force 0.1 ampere through the cell. The current density thus obtained was approximately ten times that used in copper refining. Later Kahlenberg<sup>1</sup> succeeded in depositing lithium from the same solution upon an iron cathode without a diaphragm and consequently requiring only about one-tenth the voltage used by the former experimenters. He emphasized the alloying effect exerted by the iron cathode.<sup>3</sup>

There is a widely prevalent idea that the decomposition point<sup>4</sup> is definite even to the hundredth of a volt.<sup>5</sup> Such an im-

<sup>1</sup> Jour. Phys. Chem. 4, 349 (1900); 3, 602 (1897).

<sup>2</sup> Zeit. Electrochemie 4, 290 (1897).

<sup>3</sup> The Role of Water, Etc. (Abstract — original article in preparation.) Patten and Mott. Electrochem. Industry, 1, 417 (1903).

<sup>4</sup> Le Blanc has defined the decomposition point as that voltage at which a steady current just begins to flow through the electrolyte. His method of extending the line to the X axis does not involve the CR line as suggested by Bancroft.

<sup>5</sup> Cf. S. L. Bigelow. Jour. Phys. Chem. 6, 603 (1902); Ibid. May (1903).

pression is likely to be received from the treatment of the subject given in Le Blanc's *Electrochemistry*. A short discussion<sup>1</sup> of this point is given in a former paper.<sup>2</sup> This conception of a definite decomposition point has been connected with the assumption of one single chemical reaction when a solution is electrolyzed. The fallacy of such an assumption is clear, since the reactions which take place at anode and cathode are largely dependent upon the current density. The importance of current density as a factor in decomposition point determinations will be developed below.

The experimental results are presented in the order of the series, thus giving the effect of a  $\text{CH}_2$  increment upon the process of electrolysis. Allyl alcohol served to show the variation due to an unsaturated group; glycerine, a typical polybasic alcohol; and phenol, an aromatic hydroxyl compound.

#### Lithium chloride in water

In Table II are given the values for a fairly concentrated (32.93 percent) solution of lithium chloride in water. Column I contains the total voltage, which represents the reading on a good Jewell voltmeter less the CR drop across the resistance  $R$ , as given in Figs. 1 and 2 and described in connection therewith. In column II is shown the voltage to which the corresponding value in column I has changed after a period of ten minutes. Column III gives some independent readings of the voltage across the cell taken on the potentiometer (given in Fig. 2). In column IV the polarization of the anode referred to Ostwald's

<sup>1</sup> The discussion between Wiedeburg, *Zeit. phys. Chem.* 14, 174 (1894); *Wied. Ann.* 51, 302 (1894), and Le Blanc, *Zeit. phys. Chem.* 13, 165 (1894), is of interest in this connection. See also Pellat, *Comptes rendus*, 103, 1238 (1889).

<sup>2</sup> Patten and Mott. *Trans. Am. Electrochem. Soc.* 3, 317 (1903). Consult further Le Blanc. *Zeit. phys. Chem.* 8, 299 (1891). L. Glaser. *Zeit. Electrochemie*, 4, 355, 373, 397, 424 (1897-1898). Emil Bose. *Ibid.* 4, 153 (1898). W. D. Bancroft. *Jour. Phys. Chem.* 5, 133 (1898). J. W. Langley. *Trans. Am. Electrochem. Soc.* 2, 255 (1902). W. M. Johnson. *Electrochem. Industry*, 1, 373, 454, 537 (1903). Karl Elbs. *Übungsbeispiele für die Elektrolytische Darstellung chemische Präparate* (Wilhelm Knapp, Halle a. s. 1902) and literature given there. C. P. Townsend. *Electrochem. Industry*, 1, 535 (1903).

zero<sup>1</sup> is given. To this zero, also are referred the values of the cathode polarization in column V.

TABLE II.  
Lithium Chloride in Water  
(32.93 percent solution.) Temp. 23.8° C.

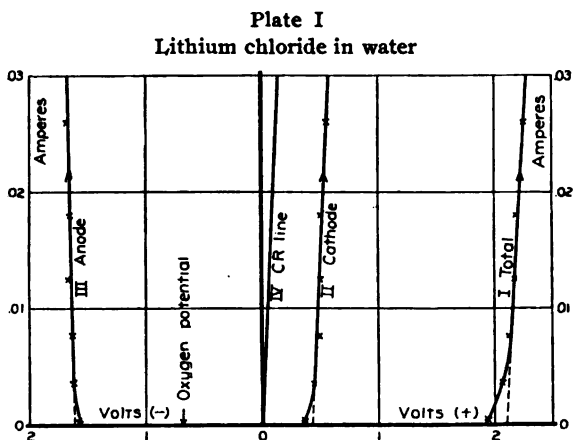
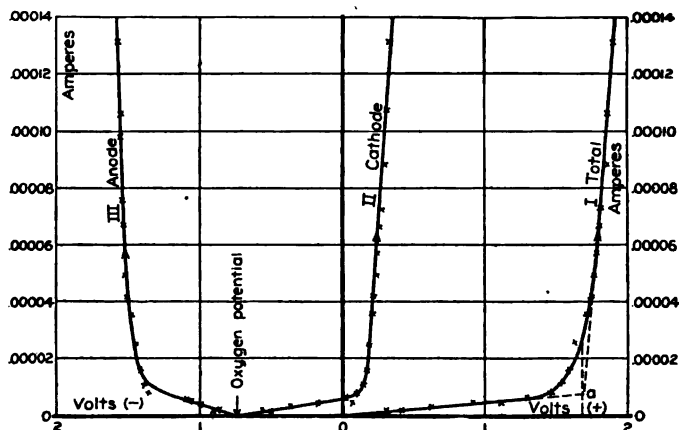
Volts						Amperes		
Total I.	Total II.	Total III.	Anode IV.	Cathode V.	Total VI.	VII.	VIII.	IX.
0.32	—	0.30	—0.87	—0.56	0.31	0.00000197	—	—
0.48	—	0.49	—0.91	—0.49	0.42	0.00000157	—	—
0.62	0.66	0.65	—0.99	—0.36	0.63	0.0000079	0.0000035	—
0.90	0.95	0.95	—1.09	—0.17	0.92	0.0000099	0.0000047	—
1.11	1.15	1.10	—1.06	+0.07	1.13	0.0000087	0.0000047	—
1.24	1.34	1.30	—1.27	+0.03	1.30	0.0000157	0.0000063	—
1.45	1.52	1.45	—1.36	+0.10	1.46	0.0000153	0.0000079	—
1.54	1.59	1.53	—1.39	+0.15	1.54	0.0000157	0.0000110	—
1.63	—	1.59	—1.42	+0.17	1.59	0.0000169	0.0000157	—
1.65	1.65	1.63	—1.44	+0.19	1.63	0.0000251	0.0000251	—
1.72	1.74	1.71	—1.48	+0.23	1.71	0.0000378	0.0000354	—
1.79	—	1.74	—1.51	+0.24	1.75	0.0000414	0.0000402	—
1.71	—	1.78	—1.53	+0.24	1.77	0.0000492	—	—
1.73	—	1.79	—1.53	+0.24	1.77	0.0000571	—	—
1.84	1.84	1.81	—1.54	+0.26	1.80	0.0000658	0.0000658	—
1.87	1.88	1.83	—1.53	+0.28	1.81	0.0000729	0.0000721	—
1.89	1.89	1.85	—1.56	+0.30	1.86	0.0000887	0.0000887	—
1.94	—	1.87	—1.55	+0.31	1.86	0.0001062	—	—
1.89	—	1.88	—1.57	+0.33	1.90	0.000131	—	—
1.90	1.91	1.89	—1.57	+0.32	1.89	0.000150	0.000149	—
1.90	1.90	1.91	—1.57	+0.34	1.91	0.000199	0.0001995	—
1.92	—	1.93	—1.574	+0.346	1.92	0.000248	0.000250	—
1.93	—	1.93	—1.576	+0.358	1.93	0.000301	0.000297	—
2.04	—	2.07	—1.62	+0.45	2.07	0.00362	0.00362	0.004
2.13	—	2.13	—1.63	+0.49	2.12	0.00765	0.00769	0.008
2.15	—	2.13	—1.66	+0.49	2.15	0.0122	0.0126	0.0125
2.17	—	2.19	—1.66	+0.49	2.15	0.0183	—	0.018
2.23	—	2.25	—1.68	+0.55	2.23	0.0267	—	0.026
2.26	—	2.30	—1.70	+0.59	2.29	0.0364	—	0.035
—	—	—	—1.72	+0.63	2.35	—	—	0.045

Column VI gives the total voltage of the cell as calculated

<sup>1</sup> The normal calomel electrode taken as —0.56 volt.



from the algebraic difference of the anode polarization (column IV) and the cathode polarization (column V). Columns I, II, III, and VI check each other reasonably well, especially on taking into consideration the influence of the time factor. The current as first taken is given in column VII and the reading for the current after ten minutes is given in column VIII. The current as given by the milliammeter appears in column IX.



The above data is graphically represented in plates I and II. Since the current varies from 0.000005 ampere to 0.045

ampere, we have found it necessary to use two scales, one a hundred times the other. In plate I, curves I, II, III, represent respectively the total polarization, the cathode polarization and the anode polarization. For this scale the CR line is not drawn, for the reason that it is nearly parallel to the Y axis. In plate II the curves are numbered as in plate I, and in addition, curve IV represents the total CR drop.<sup>1</sup>

TABLE III.  
(15.84 percent solution.) Temp. 25° C.

Volts	Amperes	Volts	Amperes
1.98	0.001	2.58	0.106
2.18	0.017	2.78	0.161
2.38	0.058	2.98	0.216

In Table III and plate III are shown the readings and decomposition curve for lithium chloride (15.84 percent) in water. The large change in concentration from the first aqueous solution is not greatly in evidence in the voltage required to decompose the solutions. The conductivity of this second solution is not greatly different from that of the first solution—the point of maximum<sup>2</sup> conductivity lies at a percentage between that of the two solutions used.

*Residual Currents.*—The study of anode and cathode curves with regard to residual currents affords a clue to the independent reactions that take place at the respective electrodes.

<sup>1</sup> In the preceding plates only one zero is used. Curve I, the total curve for the cell, takes its origin here. The reason the anode and cathode curves start at  $-0.83$  volt and not at  $0.0$  volt is that before impressing an E. M. F. upon the cell, each platinum electrode exhibits the same single potential toward the solution—due to oxygen, as explained in the text—i. e.,  $-0.83$  volt. The total curve (I) may be checked by adding the anode (curve III) value for any given current to the cathode (curve II) value for the same current. In plate I no CR line is indicated by the slope of the straight portions of curves I, II, and III. Reference to plate II, curve IV, gives the CR line for this solution. It is essential that the reader bear in mind the scale to which these curves are plotted.

The above points are stated in the text, but it is considered best to emphasize them for the sake of clearness.

<sup>2</sup> Landolt and Börnstein. Physical Tables, 1894.

In plate I it will be noticed that the anode and cathode curves start from a common point, as they must if there is a current density at which the polarization is zero. This common point represents the single potential of both electrodes, due to the oxygen dissolved in them and in the electrolyte. The value of this single potential for this solution is  $-0.83$  volt. With very large cell resistance, which means a small current with a large fall of potential, the CR-drop lines of the anode and cathode curves pass through this common point and the CR line for the cell as a whole passes through zero, since the cell offers very

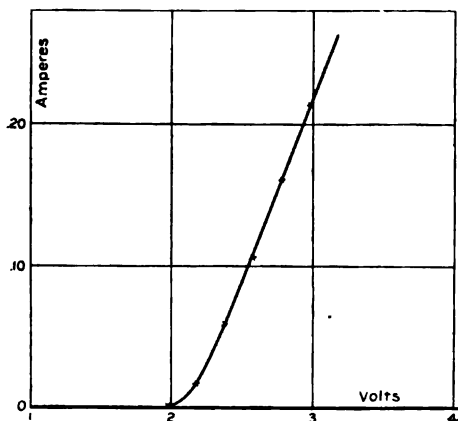


Plate III  
Lithium chloride in water

little polarization. In our curves the CR-drop across the solution is very small, as the cell resistance was about four ohms. It is of interest to note the relative rate of increase of the anode and cathode curves. One would expect the anode curve to rise much faster than the cathode, since it is assumed that the oxygen can depolarize only at the cathode; but these two curves show no striking difference in this respect; however, the cathode curve lags a little behind the anode curve.

*Anode Curve.* — This curve is the resultant of many reactions at the anode. Undoubtedly, reactions similar to those in sodium chloride take place with the consequent formation of various chlorine oxy-salts of lithium, depending on the current

density, as well as upon other conditions. In a previous paper,<sup>1</sup> we calculated the single potential of chlorine for *dilute* aqueous solution as  $-2.00$  volts. As this single potential is above that of oxygen when it is electrolyzed from acid solution, on electrolyzing dilute, aqueous hydrochloric acid, not chlorine, but oxygen is given off; but a concentrated solution of hydrochloric acid gives off chlorine upon electrolysis. For these, the calculated single potential of chlorine is much less than for dilute solutions. The heat of dilution of  $\text{HCl} + 2.50 \text{H}_2\text{O}$  is  $4.47$  large calories. Many of the so-called experimental determinations of the single potential of chlorine are determinations of the single potential of oxy-compounds of chlorine.<sup>2</sup> It is not our purpose to discuss anode reactions in this paper.

*Cathode Curve.*—Three sets of reactions at the cathode represent three stages in the electrolysis of alcohol solutions of lithium chloride. The usual residual current phenomenon constitutes the first stage. Here the dissolved gases depolarize the products of electrolysis. The second stage involves the liberation of hydrogen and the formation of *lithium alcoholates*. The third stage gives the primary product of electrolysis. The metallic lithium plates out at the proper current density. We could, from the standpoint of the third stage, regard the second as residual current phenomena in which the products of electrolysis are partially depolarized by chemical action upon the solvent.

In aqueous solution, we have the first two stages, and the third in a modified form. The first stage was discussed under residual current. In the second stage, the lithium as fast as liberated acts upon the water with the evolution of hydrogen and the formation of lithium hydrate. The single potential of hydrogen in alkaline solution is generally taken as  $+0.527$  volt. The polarization at the cathode in this aqueous solution of lithium chloride is seen to be lower than the value  $+0.527$  volt. Perhaps this comes in part from the tendency of lithium chloride

<sup>1</sup> *Electrochemical Industry*, Sept., 1903.

<sup>2</sup> Erich Müller. *Zeit. Electrochemie*, 6, 573, 581 (1900).

to form oxy-chlorides in aqueous solutions. This would furnish partial depolarization.

Certain metals exert an alloying effect upon the deposition of alkali metals from solution. It is to this phenomenon that we refer when we speak of the third stage of electrolysis as proceeding in a modified form in aqueous solutions. Mercury has received much study as a cathode metal in the production of alkali metals. Sack<sup>1</sup> and F. Haber<sup>2</sup> have found that certain other metals will alloy to a greater or less degree.

*Primary Electrolysis.*—Le Blanc<sup>3</sup> and others have advocated the primary electrolysis of water. On the other hand, Sack<sup>4</sup> and F. Haber<sup>5</sup> have held to the contrary theory and have advanced the strong argument that the separation by the alloying<sup>6</sup> effect of alkali metals to form amalgams, metal clouds, etc., proves that the solute furnishes the primary products. This argument is further borne out by our results where the alloying effect is eliminated by using an indifferent electrode. We obtained from the alcohol solutions lithium in an *unalloyed* form. From this we derive the general proposition that the primary products do not come from the water, alcohol, ketone, pyridine, or other solvent, but from the conducting solute.

*Decomposition Curves.*—Considerable doubt prevails as to the proper treatment of decomposition curves. Le Blanc's method leaves too many elements of uncertainty for it to be entirely satisfactory. The theory that upon electrolyzing a solution containing a binary solute there is one definite voltage of decomposition and only one definite reaction, is misleading, as was stated previously. In the arrangement of apparatus described by Lorenz<sup>7</sup>, no definite size of either electrode<sup>8</sup> is given ;

<sup>1</sup> Sack. *Zeit. anorg. Chem.* 7, 226, 352 (1903).

<sup>2</sup> F. Haber. *Trans. Am. Electrochem. Soc.* 2, 189 (1903).

<sup>3</sup> Le Blanc's "Electrochemistry," pp. 259, 265.

<sup>4</sup> Loc. cit. above.

<sup>5</sup> Loc. cit. above.

<sup>6</sup> The Alloying of Metals as a Factor in Electroplating. L. Kahlenberg. *Electrochem. Ind.* 1, 6, 201 (1903). Physical Character of Metal Deposits. C. F. Burgess and C. Hambuechen. *Ibid.* 1, 6, 204 (1903).

<sup>7</sup> Loc. cit.

<sup>8</sup> See writings of Fromme, Glaser, Müller, and others concerning the effect of electrode area upon polarization.

the required sensibility of the galvanometer is left indefinite; and, in fact, it is recommended to plot simply the deflection of the galvanometer, instead of the current or current density. We have made a calculation of the probable current density really used, under ordinary conditions, in such an arrangement. Our calculations gave the relatively large current density of about one milliamperere per square centimeter. Since the current density is not considered to be a factor, of course the selection of a proper scale for plotting the results is not thought to be essential. To show that the scale may be of great importance, attention is called to the fact that the curves on plate I are plotted to a current scale 100 times greater than that used for those on plate II. Another point usually left indefinite, is the resistance of the cell. The importance of this point is seen to be still greater in view of the C R lines passing through zero, which may be gotten with cells of very great resistance. Moreover, upon this resistance depends the maximum current density that can be obtained with moderate voltages. Finally, all these variable factors are eliminated by using known current densities.

Wiedeburg's method of obtaining decomposition points is illustrated in plate I. Two points are selected on each side of the place of maximum curvature. Straight lines are drawn through these points and the intersection is taken as the desired decomposition point.<sup>1</sup> By this excellent method more than one decomposition point may be determined. (Le Blanc's method gives theoretically but one decomposition point.) In working with the total voltage, the rate of change is a complex quantity, being the sum of the rates of change of the two independent polarizations, at the anode and at the cathode. The current density, too, is not given the place it deserves in this method.

Consideration of current density is essential, also, in taking discharge potentials.<sup>2</sup> Curves of impressed voltage and discharge potential should be considered in the light of voltage absorbed in CR drop which depends on size and form of cell and electrodes,

<sup>1</sup> Glaser. *Zeit. Electrochemie*, 4, 397 (1897-1898).

<sup>2</sup> Langley. *Trans. Am. Electrochem. Soc.* 2, 255 (1902).

and in the light of the variations in the products of electrolysis at different current densities. At moderate current densities, we have obtained discharge potentials close to four volts on electrolyzing lithium chloride in amyl alcohol. At somewhat lower current densities the discharge potential was a little over two volts.

To eliminate these factors of uncertainty and to broaden our view of the phenomena, the values of polarization will be given for current densities which differ successively by the logarithmic factor ten. The CR drop across the cell is subtracted in each case. Graphically, this is equivalent to extending the CR line to its intersection with the X axis (the abscissæ along which volts are plotted). This method applies to anode and cathode curves as well as to the curve for the total cell. We give the results of our calculations in Table IV on the (32.93 per cent) solution of lithium chloride in water.

TABLE IV.

I. Current	II. Current density	III. Total	IV. Anode	V. Cathode
0.0000003	0.0000001	0.06	-0.88	-0.82
0.000003	0.000001	0.66	-0.96	-0.30
0.00003	0.00001	1.70	-1.49	+0.21
0.0003	0.0001	1.93	-1.576	+0.358
0.003	0.001	2.07	-1.62	+0.45
0.030	0.010	2.20	-1.70	+0.50

Table IV shows the effect of variation in current density upon the polarization of the total cell and, at each electrode. Column I contains the total current passing through the cell. Dividing the value of the current in column I by 3, the area in square centimeters of the electrodes, gives the current per square centimeter, which is shown in column II. The total polarization of the cell is given in column III, while columns IV and V show the anode and cathode polarization for the same current density.

In this Table IV, it is shown that a change of current density from 0.00001 ampere per square centimeter to 0.001, in-

creases the polarization of the total cell from 1.70 to 2.07 volts. The CR drop of the cell for both these current densities is practically negligible. At current densities above 0.010 amperes per square centimeter, the voltage absorbed by the resistance of this cell, for this solution, rapidly increases so that the much smaller increase in polarization becomes negligible and the true CR line of the cell appears.

### Ethyl alcohol

Absolute ethyl alcohol from Kahlbaum was used as solvent.

TABLE V.  
Lithium Chloride in Ethyl Alcohol  
Temp. = 25° C.

Volts	Amperes	Volts	Amperes
0.96	0.00002	6.85	0.109
1.55	0.00043	7.85	0.133
1.75	0.00123	8.85	0.159
2.53	0.00454	9.85	0.183
2.98	0.013	10.85	0.206
3.35	0.025	11.85	0.230
3.85	0.035	12.85	0.252
4.35	0.050	13.85	0.274
4.85	0.060	14.85	0.294
5.85	0.084		

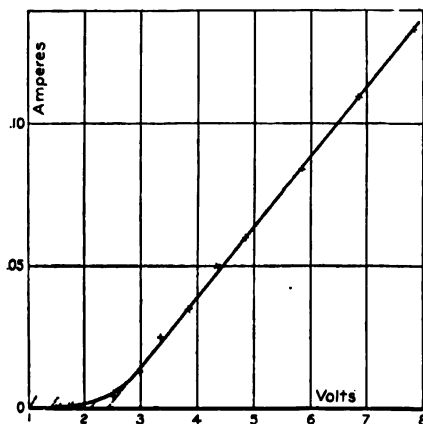


Plate IV  
Lithium chloride in ethyl alcohol



Readings on the current E. M. F. curve are given in Table V and plotted on plate IV. These readings were checked by three other sets.

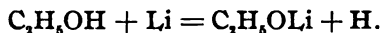
The decomposition curve of the ethyl alcohol solution is quite similar to the curves obtained for aqueous solutions. This curve differs (at these current densities) from the curves obtained with the higher members of the carbinol series. Even at a current density of about 0.300 ampere per square centimeter (or 280 amperes per square foot) there is no evidence of lithium coming out. A grey coating, not of metallic lithium, forms upon the cathode. After electrolyzing at high current density (about 0.300 ampere per square centimeter) for two and one-half hours, this grey coating had formed to a thickness of over one millimeter. This increased the resistance of the cell so that the CR line of the current E. M. F. curve approached more closely to the X axis. The increase in resistance is largely due to this insulating coating and but slightly to the stripping of the solution. As no good evidence for the deposition of lithium appeared at any of these current densities, an extremely high current density was tried.

A fine platinum wire, immersed about two centimeters in the solution, served as cathode. It is well to use some metal that does not alloy with the alkali metal. Mercury, tin, lead, etc., will not serve as cathode metals for obtaining the unalloyed alkali metal, but platinum is an excellent metal for this purpose, since it is quite indifferent. This cathode was placed about two centimeters from the anode, a large platinum plate. A 110-volt direct current circuit was connected in, with proper protection, such as fuses, or lamps in series. Under these conditions the lithium came out, for on immersing the cathode in water, hydrogen was evolved. This experiment was successfully repeated several times.

Since an ethyl alcohol solution of lithium chloride requires such enormous current densities (over 500 amperes per square foot) to get even a trace of lithium in unalloyed form, we may

expect methyl alcohol (from its position in the carbinol series)<sup>1</sup> to require even higher current densities.

At the cathode for moderately high current densities, in ethyl alcohol solutions, all the lithium is used up by the solvent according to the well known reaction:—



We have observed the discharge potential for a current density of about 0.010 ampere per square centimeter. The value found was + 0.50 volt. This value was not particularly different from the single potential of hydrogen in aqueous alkaline solutions. This value will be used later in calculations upon the single potential of metallic lithium.

At the anode free chlorine is not given off but various chlor-alkyl compounds are formed.

The formation of hydrochloric acid, acetic acid, etc., by the further oxidation of the alcohol lowers the efficiency at the cathode through diffusion and makes the use of a diaphragm desirable.

The specific conductivity<sup>2</sup> of this ethyl alcohol solution was found by the Kohlrausch method to be  $4.24 \times 10^{-4}$  at 22.8° C.

### Propyl alcohol

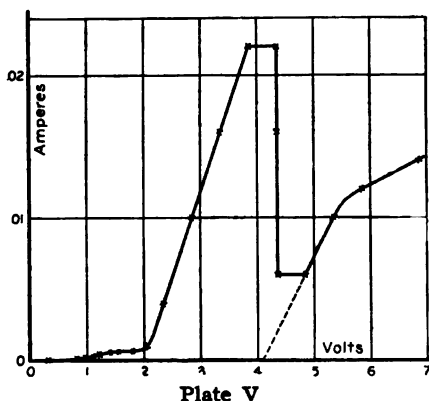
The data for a solution of lithium chloride (3.72 percent) in propyl alcohol is given in Table VI and plotted in plate V. The lower part of the curve is not very different from the curves for aqueous or ethyl alcohol solutions. The apparently large residual current, observed below 1.5 volts comes, in part, from the difference of the scales. The curves on plates I are plotted to a scale of 1/200 of that used here.

<sup>1</sup> Assuming a rate of action of metallic lithium upon water such that one-tenth of a gram of lithium is dissolved from one square centimeter by the water in one minute, the current density required to furnish this lithium would be 22.8 amperes per square centimeter or 21200 amperes per square foot. This current density is, roughly, fifty times that required for ethyl alcohol solution.

<sup>2</sup> Fitzpatrick. *Phil. Mag.* [5] 24, 377 (1887). Völlmer. *Wied. Ann.* 52, 328 (1894). Zelinsky and Krapivin. *Zeit. phys. Chem.* 21, 35 (1896). Harry C. Jones. *Zeit. phys. Chem.* 31, 114 (1899). Jones and Lindsay. *Am. Chem. Jour.* 28, 329 (1902). A. T. Lincoln. *Jour. Phys. Chem.* 3, 457 (1899).

TABLE VI.  
Lithium Chloride in Propyl Alcohol  
Temp. = 24° C.

Volts	Amperes	Volts	Amperes
0.30	0.0000119	2.35	0.004
0.76	0.0000276	2.85	0.010
0.82	0.000167	3.35	0.016
0.97	0.000217	3.85	0.022
1.09	0.000296	4.35	0.022
1.20	0.000387	4.35	0.016
1.29	0.000490	4.35	0.006
1.40	0.000582	4.85	0.006
1.55	0.000630	5.35	0.010
1.84	0.000645	5.85	0.012
2.05	0.000938	6.35	0.013
		6.85	0.014



Lithium chloride in propyl alcohol

At a current of 0.022 ampere (a current density of 0.007 ampere per square centimeter) the reaction at the cathode changes and some of the lithium remains in spite of the action of the solvent, and its counter E. M. F. causes the observed increase in polarization (about two volts rise). This causes a decrease in the current, as the voltage previously absorbed in the CR drop is now used to overcome the excess counter E. M. F. If we know the cathode polarization, with hydrogen coming off and no lithium being plated out, then the

single potential of the metallic lithium may be obtained by adding this rise of about two volts to the single potential of hydrogen in the lithium alcoholate solution.

By the method used with ethyl alcohol for getting higher current density, we obtained a good coating of lithium upon platinum. It gave off hydrogen on dipping into water.

While the action of propyl alcohol upon the alkali metal is much less than that of ethyl alcohol, yet, with moderate current densities, it is not easy to get enough metallic lithium out to obtain its discharge potential.<sup>1</sup> With solutions of lithium chloride in butyl alcohol and in amyl alcohol, we obtained the high discharge potentials due to metallic lithium. For the discharge potential of the whole cell at a current density of 0.010 ampere per square centimeter, the propyl alcohol solution gave a value of 2.3 volts. From a current density of 0.100 ampere per square centimeter the anode gave a discharge potential of -1.70 volts, and from a current density of about 0.030 ampere per square centimeter, the cathode gave a discharge voltage of +0.556 volt. This value for the cathode is higher than the single potential of hydrogen in alkaline solutions. It probably means that a small amount of metallic lithium only partially covers the platinum electrode and so has less effect upon the discharge potential.

The lack of agreement between the upper CR line and the lower CR line for propyl alcohol, plate V, is due to the formation of a film upon the cathode. This increase in resistance causes the tilt noticed in the upper CR line.

The specific conductivity of this solution as obtained by the Kohlrausch method was  $19.20 \times 10^{-4}$  at 22.8° C. References and work on conductivity and allied phenomena in propyl alcohol solutions may be found among the writings of Schlamp and of H. C. Jones. The propyl alcohol solution has about one-

<sup>1</sup> At the break-point in the current E. M. F. curve where lithium is being deposited, and for short distances up the CR line beyond this point, the quantity of lithium is so small and is so quickly dissolved away by the solution that a discharge potential must be taken with great rapidity. See curve II, plate X.

half the conductivity of the ethyl alcohol solution, although 50 percent more lithium chloride is dissolved in the propyl alcohol.

The current density required to obtain lithium from propyl alcohol is considerable less than one-tenth the current density required to obtain lithium from ethyl alcohol solution.

In the next higher number of the carbinol series, the required current density is again reduced more than ten times.

#### Butyl alcohol

The data for lithium chloride (9.56 percent) in butyl alcohol is to be found in Table VII and plate VI. The lower part of

TABLE VII.  
Lithium Chloride in Butyl Alcohol  
Temp. = 24° C.

Volts	Amperes	Volts	Amperes
0.57	0.00000?	2.90	0.00151
0.97	0.00000?	3.36	0.00162
1.14	0.000083	4.51	0.00112
1.30	0.000127	3.90	Discharge voltage
1.31	0.000154	5.85	0.003
2.05	0.000791	7.85	0.006
2.40	0.00151	9.85	0.011
2.48	0.00125	11.85	0.014

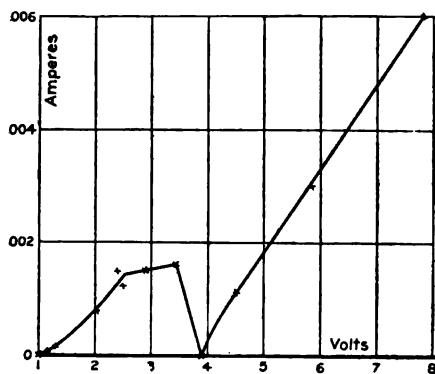


Plate VI

Lithium chloride in butyl alcohol

the curve corresponds to the curve obtained in water. The

residual current flowing below two volts is of no greater magnitude than the residual current in the solution already considered. The scale to which this curve is plotted is greater than that used in plotting the curve for the propyl alcohol solution.

Butyl alcohol is remarkable for the low current density at which, together with hydrogen, some metallic lithium comes out. This current density is about one-twentieth the current density used in electrolytic copper refining. At about half the current density used in refining copper, we obtained a good smooth coating of lithium, particularly heavy at the edges of the platinum cathode. The action of the butyl alcohol upon the lithium was so slow that when we emptied the cell and, after some minutes, added water, a considerable evolution of hydrogen took place.

We obtained readings for discharge potential as follows: 4.05 volts and 3.9 volts. The discharge potentials of anode and cathode were not taken as the solution had considerable resistance, and consequently required a more delicate zero instrument than the one at our disposal.

Upon continued electrolysis, the resistance of the cell increased, as was observed with the other alcohol solutions. Some very peculiar curves are obtained owing to a cathode film.

The specific conductivity of the solution used was  $5.67 \times 10^{-4}$  at 22.8°. This is about one-sixth of the conductivity observed for the propyl alcohol solution, although considerably more than twice as much lithium chloride is dissolved.

#### **Amyl alcohol**

Amyl alcohol is discussed in detail as presenting the phenomena attendant upon the deposition of an alkali metal from an alcohol more fully than the other alcohols taken up in this paper. Table VIII gives the current E. M. F. curve for a solution (4.77 percent LiCl) containing a little water. As plotted in plate VII, the curve is seen to be of the usual form. The discharge potential of 3.85 volts afford good evidence that lithium came out. At a high current density lithium was deposited upon platinum in such quantity that it could be cut with a knife.

TABLE VIII.  
Lithium Chloride in Amyl Alcohol  
Temp. = 25.5° C.

Volts	Amperes	Volts	Amperes
1.69	0.000263	3.84	0.0100
2.04	0.000810	4.84	0.0100
2.50	0.0033	5.84	0.0114
3.14	0.0072	3.85	Discharge potential

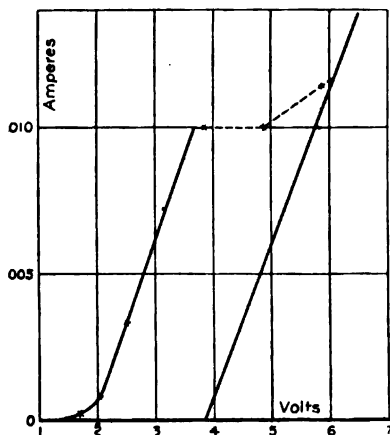


Plate VII  
Lithium chloride in amyl alcohol

On testing with water, copious evolution of hydrogen took place. Table IX shows the increase of cell resistance of the same solu-

TABLE IX.  
Lithium Chloride in Amyl Alcohol  
Temp. = 22° C.

Volts	Amperes	Time. Min.	Volts	Amperes	Time. Min.
6	0.011	0	50	0.055	—
6	0.008	1	55	0.055	—
9	0.006	3	70	0.059	5½
15	0.018	4	75	0.050	6
20	0.025	—	80	0.053	—
30	0.044	—	88	0.060	—
35	0.050	—	100	0.090	—
40	0.053	—	100	0.140	10
45	0.057	—	—	—	—

tion upon continued electrolysis. A film on the cathode, comparable to that which forms in acetone, ethyl, and propyl alcohol solutions under like conditions, is responsible for this high resistance. The alcohol used for this solution boiled near  $120^{\circ}\text{C}$ .

By distilling another sample of amyl alcohol a portion was gotten fairly dry. With this a solution containing 8.26 percent LiCl was prepared, and the determinations given in Tables X, XI, XII, and XIII were made.

TABLE X.  
Lithium Chloride in Amyl Alcohol  
Temp. =  $29^{\circ}\text{C}$ .

Volts	Amperes	Volts	Amperes
0.55	0.0000146	4.68	0.00418
0.83	0.0000720	5.54	0.00527
1.02	0.000127	6.54	0.00595
1.21	0.000160	7.36	0.00686
1.28	0.000258	3.8	Discharge potential
1.78	0.00074	10.0	0.010
2.51	0.00121	8.0	0.0067
3.24	0.00219	6.0	0.0040
3.71	0.00286	—	—

TABLE XI.  
Lithium Chloride in Amyl Alcohol  
Temp. =  $29^{\circ}\text{C}$ .

Volts	Amperes	Volts	Amperes
1.92	0.00081	8.69	0.0091
2.49	0.00108	10.73	0.0127
3.28	0.00216	8.26	0.0084
2.83	0.00369	6.78	0.0052
4.31	0.00391	5.67	0.0038
5.03	0.0047	4.88	0.00175
6.14	0.0046	3.97	0.000270
7.37	0.0064	3.90	Discharge potential

The above tables are duplicates for the same solutions, and



their close agreement is evident from plate VIII, which is plotted from table X, and plate IX, giving the graph of Table XI.

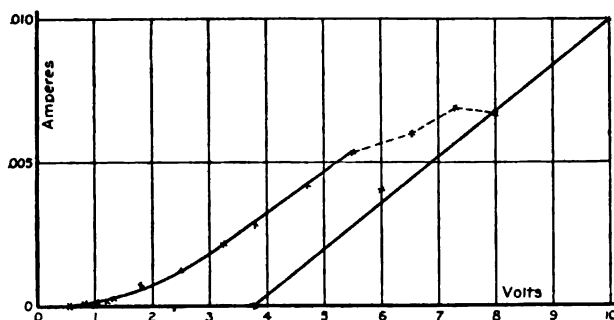


Plate VIII  
Lithium chloride in amyl alcohol

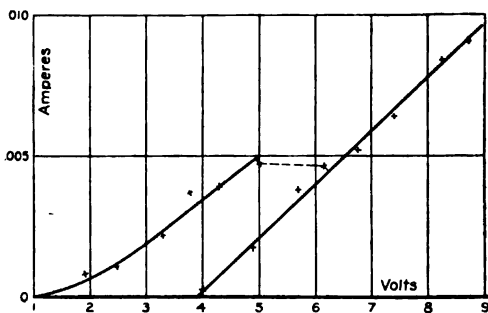


Plate IX  
Lithium chloride in amyl alcohol

Before discussing these curves the data and chart given in Tables XII and XIII and plate X should be considered.

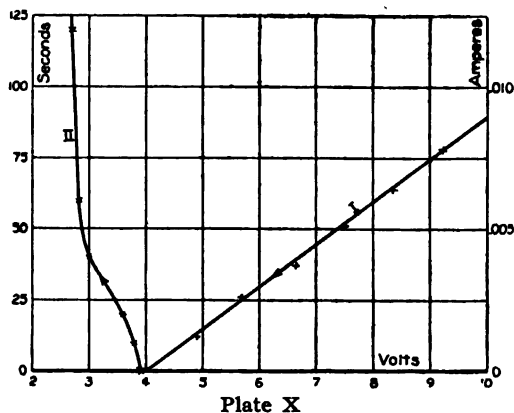
TABLE XII.  
Lithium Chloride in Amyl Alcohol  
Temp. = 29° C.

Volts	Amperes	Volts	Amperes
9.22	0.0078	5.74	0.0026
8.36	0.0064	4.88	0.0012
7.49	0.0051	3.90	Discharge
6.63	0.0037	—	—

TABLE XIII.

Discharge Potential of Cell after Electrolyzing about Ten Minutes

Volts	Seconds	Volts	Seconds
3.9	(about) 1	2.7	120
3.8	10	2.67	180
3.6	20	2.67	240
3.0	40	2.50	540
2.8	60	—	—



Lithium chloride in amyl alcohol

I. Current E. M. F. curve. II. Time curve of discharge voltage

Table XII contains the current E. M. F. curve obtained by starting at 9.22 volts pressure and gradually decreasing the voltage till 4.88 volts are reached. This set of readings is plotted in curve I. When the external pressure is removed from the cell and, at the instant of release, the voltage (counter E. M. F.) of the cell is taken, 3.90 volts, the first reading given in Table XIII is obtained. At intervals, other readings showed a general decrease in this polarization, counter E. M. F., or battery effect—as it is variously termed. Curve II is drawn from the data in Table XIII, the ordinates being in seconds. For curve I the readings were made quickly in order to get the true CR line, and for curve II the intervals are given in Table XVII. Curve II has its origin very near the foot of curve I, showing that the transfer resistance is small,—this is emphasized by the fact that

the discharge potential, 3.90 volts, would have been higher if the reading had been taken more rapidly.<sup>1</sup>

This rapid decrease of polarization shows the necessity of taking discharge potentials with great rapidity if one is to use the reading as a criterion for the deposition of a metal upon the cathode. Especially is this so at low current densities.

The resistance of the solution used in Table VIII as taken from the CR line of plate VII is 189 ohms in the cell used throughout this work. The resistance of the nearly anhydrous solution with which Table X was determined is seen from plate VIII to be 625 ohms for the upper CR line, and very nearly the same value for the lower CR line, thus showing that the solution conducts equally well above and below the polarization values at which the solute is decomposed.<sup>2</sup>

This second<sup>3</sup> solution has a conductivity one-third less than that of the first which contained some water, as is further shown by its low boiling-point. Comparison of plates VII with plates VIII and IX, shows that the current density required to balance the action of the solution upon the deposited lithium is lower with less water present — as might be expected.<sup>4</sup>

There is a difference of 2.5° C in the temperatures for Tables VIII, IX, and X; and the concentrations were not the same, but these factors are minor compared to the effect of water in raising the conductivity and the current density requisite to plate out lithium. Consequently, while the greater resistance of the second solution occasions loss of energy as Joulean heat, the lower current density is a compensating factor.

The residual current is marked in amyl alcohol solution. With but 0.2 volt polarization a current density of  $1.0 \times 10^{-6}$

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<sup>1</sup> Considering the cell as a storage battery, it has a voltage about twice that of the lead cell, and the equivalent weight of lithium is about one-fifteenth that of the active lead.

<sup>2</sup> Compare "Single Potentials of Zinc in Aqueous Solutions," Patten and Mott. *Trans. Am. Electrochem. Soc.* 3, 340 (1903).

<sup>3</sup> This second solution contained approximately twice the percent of LiCl dissolved in the first solution.

<sup>4</sup> Compare "The Rôle of Water in the Electro-Deposition of Lithium from Pyridine and from Acetone." *l. c.*

ampere was obtained. The logarithms of the current densities are plotted against their respective voltages, in the curve, "Amyl Alcohol," given in Table XVI and plates XIV and XV. This same table (XVI) shows similar curves for the other solvents and makes clear that amyl alcohol is best adapted for study of the three stages of electrolysis discussed under the heading "Lithium Chloride in Water". At current densities less than  $1.0 \times 10^{-7}$  amperes per square centimeter, the gases liberated dissolve in the electrolyte and completely depolarize the products of electrolysis. As the current density is increased, polarization phenomena appear at about  $1.0 \times 10^{-4}$  to  $1.0 \times 10^{-5}$  amperes per square centimeter, falling off rapidly with the time when the external E. M. F. is removed. At  $1.0 \times 10^{-3}$  amperes per square centimeter, we get the usual value of the decomposition voltage. Hydrogen appears at the cathode in all of these alcohol solutions, offering a counter E. M. F. of about + 0.5 volt. The final stage in the electrolysis is reached when the current density rises to a value sufficiently high to furnish more coulombs than are required by Faraday's law for the lithium (in this particular solution), which is dissolved by the solution at a nearly constant rate.<sup>1 2 3</sup> The excess of coulombs is represented by the

<sup>1</sup> L. Bruner and St. Tolloczko. *Zeit. anorg. Chem.* 28, 317.

$$D = \frac{1}{f t} \log \frac{C}{C-x} \quad \left\{ \begin{array}{l} D = \text{constant from } \int dx = \int D_n(C-x) dt. \\ f = \text{surface exposed.} \\ t = \text{time.} \\ C = \text{concentration of saturated solution.} \\ x = \text{concentration at time, } t. \end{array} \right.$$

<sup>2</sup> We have found that sodium dissolves in anhydrous amyl alcohol and at a very constant rate; the same is true of a solution of lithium chloride in amyl alcohol, not strictly anhydrous.

<sup>3</sup> Experimental data now on hand show that while the current passing through a cell [containing an anhydrous solution of lithium chloride in amyl alcohol, with platinum electrodes] *decreases* owing to the formation of a resistance film on the cathode, the hydrogen is evolved at a nearly constant rate. This is entirely comparable to the results obtained by A. Appelberg, *Zeit. anorg. Chem.* 36, 36 (1903), in fused lead chloride, where the fused salt was shown to act upon the deposited lead at a constant rate, so that the current efficiency is a function of the current density, increasing with it till the requirements of Faraday's law are very nearly met.

$$a = 100 - \frac{K}{i^n}, \text{ where } \left\{ \begin{array}{l} a = \text{current efficiency.} \\ i = \text{current density.} \\ n = \text{power of } i. \\ K = \text{a constant.} \end{array} \right.$$

deposited metallic lithium. These considerations point very strongly to primary electrolysis: that is, to the separation of the solute into its positive and negative parts at all current densities, and to the apparently low polarization value of such separation as a consequence ensuing upon the return of energy to the circuit when these primary products act back upon the solvent.

The amyl alcohol obtained by fractioning off the water is not sufficiently anhydrous to show the true slow action of amyl alcohol upon alkali metals. For this reason the current density at which lithium came out of our amyl alcohol solution is in all likelihood higher than that needed for a strictly anhydrous solution. The butyl alcohol was from a freshly opened bottle of Kahlbaum's preparation, not dehydrated by us except in so far as standing over excess of solid lithium chloride for two months would extract the water. Judging from the very low current density at which lithium was deposited, this solution was undoubtedly very dry. Therefore it seems reasonable to attribute the higher current density necessary for the amyl alcohol solution to the presence of moisture which increased the rate at which the solution redissolved the lithium from the cathode.

The other alkali metals, potassium and sodium, at first acted vigorously upon portions of the amyl alcohol we used to make up the second solution (plates VIII and IX); but after a week's contact, only a very few small bubbles came from a large bright surface of either potassium or sodium. A slight precipitate (composition not determined) formed in both cases. The supernatant liquid had a specific resistance of  $2.4 \times 10^7$  ohms per cubic centimeter. Andrews and Ende<sup>1</sup> gave  $4.524 \times 10^7$  ohms as the specific resistance of pure amyl alcohol at 25° C.

#### Allyl alcohol

The allyl alcohol solution, 4.20 percent lithium chloride, had a higher conductivity than the other alcoholic solutions studied in this paper. The part of Table XIV represented by curve I in plate XI was taken with increasing voltages and current densities, while curve II was taken with decreasing voltages.

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<sup>1</sup> l. c.

The difference in polarization of these curves no doubt is at the anode, due to the saturation of the layer of allyl alcohol on that electrode. In some unpublished experiments on the electrolysis of zinc chloride in allyl alcohol, we observed at the anode of platinum a discharge potential of  $-1.2$  volts for the moderate current densities; and at a higher current density after electrolyzing a few minutes, the anode discharge potential was  $-1.7$  volts.

TABLE XIV.  
Lithium Chloride in Allyl Alcohol  
Temp. =  $25^{\circ}$  C.

Volts	Amperes	Volts	Amperes
0.71	0.000256	4.85	0.094
1.35	0.000622	5.85	0.164
1.70	0.00276	6.85	0.230
2.01	0.00960	7.85	0.300
2.35	0.021	3.85	0.019
2.85	0.047	4.85	0.064
3.35	0.074	5.85	0.129
3.85	0.100	6.85	0.200
3.85	0.040 after 1'	7.85	0.280

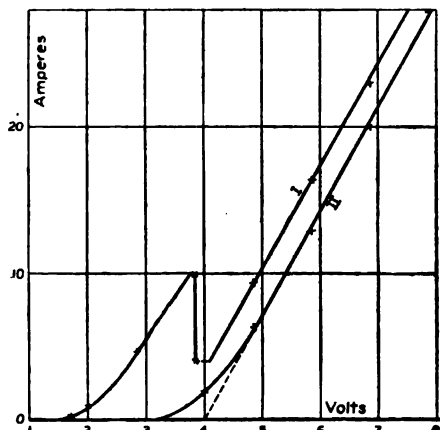


Plate XI  
Lithium chloride in allyl alcohol

Curves I and II show the counter E. M. F. of lithium at a current density of approximately 0.030 ampere per square cen-

timeter, or some 28 amperes per square foot. At quite high current density we failed to obtain enough lithium to apply further confirmatory tests.

### Glycerine

Electrolysis of a 4.14 percent solution of lithium chloride in glycerine yielded the data given in Table XV and plotted in plate XII. The curve obtained shows no polarization rise due to the deposition of metallic lithium. At very high current densities there was no satisfactory evidence of separation of lithium. The glycerine was carbonized by the Joulean heat.

TABLE XV.  
Lithium Chloride in Glycerine  
Temp. = 25° C.

Volts	Amperes	Volts	Amperes
0.46	0.0000118	5.48	0.00375
0.93	0.0000237	6.40	0.00454
1.79	0.000178	7.22	0.00534
2.44	0.000534	8.24	0.00613
3.67	0.00178	9.16	0.00692
4.57	0.00276	—	—

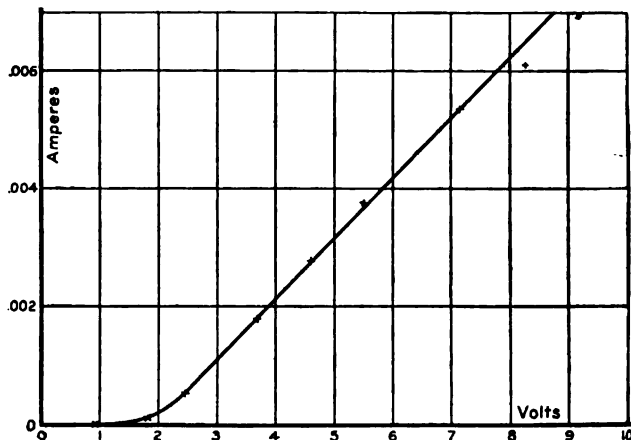


Plate XII  
Lithium chloride in glycerine

The presence of three hydroxyl groups upon only three

carbon atoms renders glycerine more like water than even ethyl alcohol, consequently these results are to be expected.

### Phenol

A solution of lithium chloride, 1.89 percent, in phenol was electrolyzed at a temperature near the melting-point of the solution,  $53^{\circ}\text{C}$ . For experimental reasons a cell different from the one used for the other solutions was taken. With platinum electrodes about three square centimeters in area and one centimeter apart, 10 volts passed 0.012 ampere, and the current E. M. F. curve<sup>1</sup> shows that increase in polarization takes place at 0.003 ampere per square centimeter.

TABLE XVI.

Lithium Chloride in Phenol

Anode — 3 sq. cm. Cathode wire — 0.003 sq. cm.

Temp. =  $53^{\circ}\text{C}$ .

Volts	Amperes	Volts	Amperes
8.48	0.0000464	3.89	0.0000097
7.59	0.0000367	2.88	0.0000105
6.69	0.0000281	1.97	0.0000244
5.77	0.0000202	1.5	Discharge
4.88	0.0000109	—	—

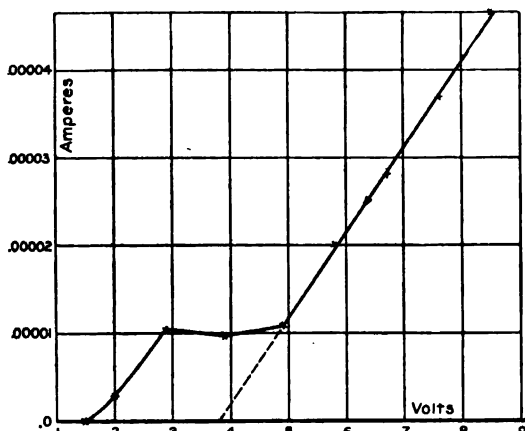


Plate XIII

Lithium chloride in phenol

<sup>1</sup> Not reproduced here since a second curve gives better insight into the phenomena.



The conductivity of this solution is of the same order as that of the glycerine solution ; our cell showed a resistance of some 4,000 ohms.

Using a cathode of fine platinum wire 0.003 centimeters in area, the data given in Table XVI was obtained. As charted in plate XIII, the curve is seen to be similar to those for butyl and amyl alcohol solutions. When the well defined CR line is produced to its intersection with the X axis, the usual polarization value, 4.0 volts, appears. For the lower part of the curve, which is also clear cut, the polarization lies near 2 volts.

It appears then that a typical phenol acts like the alcohols when used as solvent.

By way of summary, Table XVII gives the polarization values observed at different current densities for lithium chloride in the several solvents used. Column I contains the current densities in amperes per square centimeter, and under each solvents chemical formula is set the polarization corresponding to the current density in column I. These values are plotted in plates XIV and XV, using as ordinates the logarithm of the current density, and as abscissæ, the polarization in volts. These curves will be referred to later in the general discussion.

From the curves in plates XIV and XV it is to be inferred that the higher members of the carbinol series require smaller current densities for the deposition of metallic lithium. Curve

TABLE XVII.

Current density per sq. cm.	Total polarization in volts							
	H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> OH	C <sub>3</sub> H <sub>7</sub> OH	C <sub>4</sub> H <sub>9</sub> OH	C <sub>5</sub> H <sub>11</sub> OH	C <sub>6</sub> H <sub>13</sub> OH	C <sub>6</sub> H <sub>5</sub> (OH) <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> OH
0.000001	0.66	—	0.0	—	0.2	—	—	—
0.00001	1.70	1.00	0.75	1.0	0.7	—	1.0	—
0.0001	1.93	1.40	1.1	1.1	1.3	0.8(?)	1.8	—
0.001	2.07	2.10	1.8	4.0	2.0	1.8	1.9	1.9
0.010	2.20	2.40	4.0	—	4.0	2.15	—	4.0
0.100	—	4.0(?)	—	—	—	4.00	—	—
1.0	—	—	—	—	—	—	—	—

V for amyl alcohol in plate XIV was drawn in as given, contrary to the experimental data in Tables VIII to XII, because

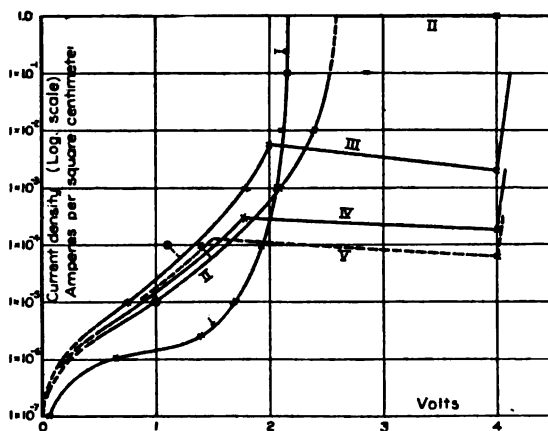


Plate XIV

Lithium chloride as solute

- |                     |                                    |
|---------------------|------------------------------------|
| I. Water            | IV. Butyl alcohol                  |
| II. Ethyl alcohol   | V. Probable curve for amyl alcohol |
| III. Propyl alcohol |                                    |

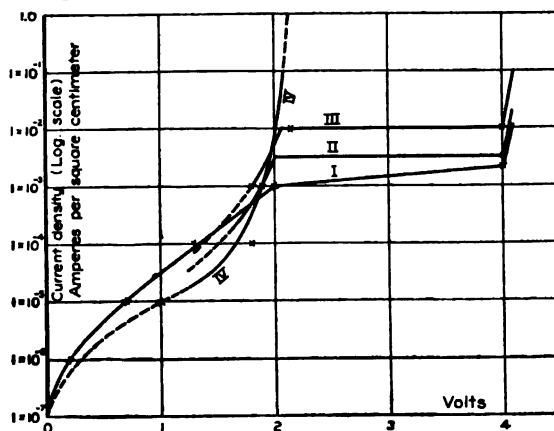


Plate XV

Lithium chloride as solute

- |                                       |                    |
|---------------------------------------|--------------------|
| I. Amyl alcohol with a trace of water | III. Allyl alcohol |
| II. Phenol                            | IV. Glycerine      |

we felt assured that this solvent was no exception to the above

general statement. Additional data now in hand shows that dehydration of the amyl alcohol over sodium and the use of an anhydrous solution justifies the curve (V, plate XIV) as originally drawn to the extent that the observed current density was as low as that required to deposit lithium from the butyl alcohol solution (Table VIII, plate VI).

#### **The single potential of metallic lithium**

The heat of formation of lithium chloride in dilute aqueous solution is 102.3 large calories. This gives 4.44 volts as the decomposition voltage of lithium chloride into lithium and chlorine. Subtracting the theoretical single potential of chlorine<sup>1</sup> gives +2.44 volts as the single potential of lithium, a little above that of potassium.

The voltages required to decompose potassium salts — nitrate, sulphate, chloride — are slightly less than those necessary for the corresponding salts of lithium. This difference is 0.05 volt. Consequently the single potential for lithium against aqueous solutions is higher than that of potassium by this same value, 0.05 volt.

Similarly, it may be shown from thermal data that the salts of zinc<sup>2</sup> are decomposed at a pressure 2.00 volts lower than the corresponding salts of lithium. On adding this 2.00 volts to the experimental value for the single potential of zinc + 0.524 volts, +2.52 volts is gotten as the single potential of lithium.

A series of metals whose single potentials have been determined experimentally, used as in the preceding paragraph to calculate the theoretical single potential of lithium, will give values for the single potential of lithium whose average approaches 2.44, the same voltage as calculated by subtracting

<sup>1</sup> Experimental Determinations of the Single Potentials of the Alkali Metals, Sodium and Potassium. Patten and Mott. *Electrochem. Industry*, Sept., 1903, Vol. I.

<sup>2</sup> The single potential of zinc against alcoholic solutions is somewhat lower than against aqueous solutions. We found the single potential of zinc against a saturated solution of zinc chloride in allyl alcohol to be +0.46 volt (Data not given). Adding this to 2.00 volts, the single potential of lithium becomes +2.46 volts. Kahlenberg has shown in several papers the influence of the heat of solutions upon the single potential.

the single potential of chlorine from the decomposition voltage of lithium chloride.

In a previous paper we calculated the single potential of lithium as + 2.00 volts from the experimental decomposition voltage of lithium chloride. It was there stated that this value was probably too low, since we assumed a polarization of - 2.00 volts at the anode. The chlorine reacts upon the solvent and the energy thus returned to the circuit lowers the single potential at the anode which rises above - 1.7 volts only with rather high current densities. In compiling Table XVIII, - 1.65 volt is used as the anode polarization.

Another point of departure for calculating the single potential of lithium is the cathode polarization value, + 0.50 volt, at which hydrogen is liberated in alkaline solution. The rise in polarization when lithium begins to deposit from lithium chloride in propyl alcohol is about 2 volts. This increase occurs only at the cathode. Adding the original + 0.50 volt at the cathode due to the hydrogen, to the two volt rise we get + 2.50 volts as the single potential of lithium.

If we subtract 1.7 volts, for chlorine, from the total polarization, 4.1 volts, the single potential of lithium is given as 2.4 volts.

Table XVIII contains several similar calculations for lithium chloride dissolved in the solvents mentioned in column 1. The rise in polarization due to the deposition of lithium is given in column 2, while the single potential of lithium obtained by adding this rise to 0.50 volt is placed in column 3. The total polarization of the cell is in column 4, and the value for the single potential of lithium gotten by subtracting 1.65 from column 4 is in column 5.

The average result of both methods gives 2.41 volts as the experimental value of the single potential of lithium. In a solution of lithium chloride in acetone<sup>1</sup> the discharge potential of the cathode on which lithium had been plated out was found

<sup>1</sup> The Rôle of Water in the Electrodeposition of Lithium from Pyridine and from Acetone. *Abstr. Electrochem. Industry*, 1, 1, 417.

to be + 2.53 volts.\* Thus the experimental values and the calculated values agree reasonably well. Some relatively slight variations may be ascribed to differences in heats of solution.

**Conditions requisite for the electrodeposition of alkali metals**

In the deposition of metals eight well known points enter : (1) The decomposition voltage ; (2) The concentration of the solution ; (3) The acid radical of the salt used ; (4) The conductivity of the solution ; (5) Current density ; (6) The substances produced at the anode and their influence on the decomposition voltage, and the possible corrosion at the anode ; (7) Chemical composition of the cathode, and possible alloying effect ; (8) Rate of action of solvent, or solution upon the metal.

TABLE XVIII.

1	2	3
Solvent	Rise	$2.00 + 0.50 = \text{S.P. of Li}$
Propyl alcohol	2.00	2.5
Butyl alcohol	2.00	2.5
Amyl alcohol	{ 2.00	{ 2.5
Allyl alcohol	{ 2.00	{ 2.5
	2.00	2.5
		Av. = 2.5
	4	5
Solvent	Total P.	Total polarization less $1.7 = \text{S. P. Li}$
Propyl alcohol	4.1	2.45
Butyl alcohol	3.9	2.25
Amyl alcohol	{ 4.0	{ 2.35
Allyl alcohol	{ 3.9	{ 2.25
	4.0	2.3
		Av. = 2.33

\* The cathode curve for lithium chloride in acetone showed a polarization of + 2.60 volts. The considerable heat of solution of lithium chloride in acetone accounts for the higher single potential as found in acetone.

These factors are closely related to each other by the fundamental and well recognized principle that the metal must be deposited by the current faster than the solution can dissolve it away. While the above conditions are known and used continually, one needs only to read current literature to appreciate that understanding of their interrelation is by no means so general. The balance between the current density plating out lithium, and the solution dissolving lithium away from the cathode is evident when called before us. *Rate* of attack is not considered definitely at first. When one meets it by raising the current density, a third relation enters: the dependence of the polarization upon the current density. Conductivity has to do with getting of high current density, and in turn concentration affects the conductivity, as well as the rate of attack upon the deposited metal.

The alkali metals are deposited, then, under the same conditions which govern other plating processes. The only difference lies in the higher voltage requisite, the greatly increased current density and the use of a solution which acts with comparative slowness upon the metal.

#### **Decomposition voltages**

Definite chemical reactions require a definite expenditure of energy. The experimental facts expressed in Faraday's law indicate the same current for all chemical equivalents, consequently the prime requisite for electrolytic separation is a voltage sufficient for the chemical work.

When aqueous solutions of many acids and alkalies are electrolyzed the anode yields oxygen and the cathode, hydrogen—the constituents of the solvent, water. The decomposition voltage of water is given by Le Blanc and others<sup>1</sup> as about 1.7 volts for polished platinum electrodes. Nevertheless zinc, manganese, iron, and other metals whose single potentials exceed that of hydrogen may be deposited from aqueous solutions of their salts. In aqueous solution it is not difficult to come at the decomposition voltage of the solvent, but for non-aqueous solu-

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<sup>1</sup> T. W. Richards and W. F. Stull. *Zeit. phys. Chem.* 42, 621 (1903).

tions it is less clear that solvent and solute are simultaneously decomposed by the passage of the current. As calculated from heat of formation data, the separation of one hydrogen from a carbon atom requires not over one volt, assuming that the hydrogen atoms bound to carbon have equal affinity. And yet the (lower) CR lines for the various alcohols when produced to their intersection with the axis of volts give a polarization which is higher than one volt; and we know, too, that the hydrogen of the hydroxyl group is replaced by the alkali metal to form alcoholates. Hydrocarbons do not act upon alkali metals at ordinary temperatures, and the activity of alcohols decreases by a logarithmic function as they approach the hydrocarbons in percentage composition. The rapidity with which this decrease in activity takes place as we ascend the alcohol series is easily understood from the increase of molecular weight, which means fewer molecules in a given volume (the specific gravity not changing greatly) while each molecule has only one hydrogen subject to replacement.

It appears then that the essential point in depositing alkali metals is to use a solvent which acts slowly upon the metal. The high heat of formation of a solvent and consequent high decomposition voltage, is thus seen to be of secondary importance.

#### **Solubility**

Saturated solutions are, generally, most desirable. For halogen salts of alkali and alkaline earth metals in alcoholic solution, the heavier the halogen, the greater the solubility. On the other hand, the solubility decreases with increasing atomic weight of the alkali or alkaline earth metal. The last statement holds also for nitrates.

#### **Acid radical**

The acid radical affects the solubility, and consequently the conductivity of the solution and the rate at which the solution acts upon the alkali metal. The anode products are, of course, directly dependent upon the radical used, and their diffusion is prevented by interposing a diaphragm.

### **Conductivity**

The solution should conduct fairly well, since in poorly conducting solutions the current density produced even by high voltage is insufficient to deposit the metal. The small quantity of electrode product which separates out with such a low current density is easily depolarized by the dissolved gases. Warburg's observation of a residual current in solutions free from gases is explained by this same consideration: that the solute is decomposed to a very slight degree, attacks the solvent, and the gases thus set free dissolve in the solution and depolarize further products of electrolysis.

For higher alcohols the increased resistance of their solutions is more than compensated by the diminished rate at which they act upon metallic lithium.

### **Current density**

Maximum current density is clearly desirable. The quantity of metal per unit area dissolved by the solution must be outweighed by the mass of metal deposited by the current.

### **Composition of the cathode**

An alloying effect at the cathode may have to do with the deposition of the alkali metals. The heat of formation of the alloy, and the rate at which the alloy is attacked by the solution from which the alkali is to be deposited, are two factors to be considered. Where the alloy is formed with liberation of heat, the energy necessary to separate the alkali metal from the solution is less. Still the heat of formation of the alkali amalgams fails to explain their formation at moderate current densities from aqueous solution.

Aqueous solutions act upon amalgams of the alkali metals more slowly than upon the metal themselves. The single potential of zinc amalgam is about the same as that of zinc alone, yet zinc is acted upon by sulphuric acid some fifty times faster than the zinc amalgam. The alloying effect is important, then, as a means of decreasing the loss of deposited metal by corrosion.

### **Conclusion**

In conclusion, this work has discussed the deposition of



lithium from carbinols, allyl alcohol, glycerine, and phenol, together with the polarization voltages required. The dependence of polarization upon the current density has been treated quantitatively. And from this treatment it appears that the process of electrolysis is essentially the same for all current densities. The residual current verges into the steady current because of the increased rate at which the solute is decomposed with increasing current density; the alkali metal, similarly, deposits on the cathode when the rate of decomposition of solute exceeds the rate of solution of the alkali metal. The low polarization in these alcoholic solutions at moderate current densities<sup>1</sup> is strong evidence<sup>2</sup> that the alcohol is not decomposed by the current simultaneously with the lithium chloride. The conductivity above and below the first break-point in the current E. M. F. curves is the same, as shown by the parallel CR lines; and, too, Richards and Landis have shown that the conduction (for residual currents in dilute sulphuric acid) is proportional to the concentration. The conclusion is, that the solute is decomposed before the solvent. It does not follow, necessarily that the solvent takes no part in the conduction. These considerations, developed for non-aqueous solutions, are applicable to aqueous solution as well.

The single potential of lithium has been determined by calculation from thermal data, by analysis of current E. M. F. curves, and by discharge potentials (both total and single) as 2.41 volts. A discharge potential (single) in a saturated solution of lithium chloride in acetone gave 2.53 volts.

It is shown that the alloying effect of the cathode used — platinum — is a minor factor in depositing alkali metals from solution, and that a solvent which acts to a considerable degree upon the metal may be preferable to one which corrodes slowly, with the formation of a high resistance film — as, for example, pyridine. High current density and consequently good conduc-

<sup>1</sup> See Table XVII, plates XIII and XIV; also plates IV to XVI.

<sup>2</sup> See discussion under "Decomposition Voltages," page 56, this article.

<sup>3</sup> *Trans. Am. Electrochem. Soc.* 3, — (1903).

tivity are essential in so far as they may be needed to balance the solvent action of the solution upon the metal. High boiling-point and latent heat of vaporization are more desirable in a solvent than very high heat of formation.

This work was done jointly in the laboratories of applied electrochemistry and of physical chemistry. The authors wish to express their appreciation of the excellent facilities accorded them by both.

*University of Wisconsin,  
Madison, Wis.,  
Jan., 1904.*

## ON THE WESTON CELL

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BY H. T. BARNES AND S. B. LUCAS

Within the last few years a great deal of work has been done with the Weston cell to show that it is equal in reproducibility and constancy to the Clark cell, and that it is in every way a suitable standard of electromotive force. The great advantage which it possesses over the Clark cell is of course the small temperature coefficient making it unnecessary, except in very accurate work, to take account of the changes of E. M. F.

Experience has shown that the small initial differences between new cells are of the same order of magnitude for the two types of cell, which gives the Clark cell a considerable advantage in point of accuracy. In physical investigation, where the measurement of temperature is usually a matter of detail, it is of little importance whether a cell possesses a small or large temperature coefficient provided it is known.

What is required of a standard is greatest possible accuracy in construction, and constancy in initial variations between different cells at all temperatures, and for a reasonable length of time. It has been shown at the Reichsanstalt, and independently in this laboratory that the Clark cell follows the temperature changes of its E. M. F. with great precision. This is shown also when the two formulas which were deduced by Kahle and by Callendar and Barnes, using different types of cells, are compared.

Callendar and Barnes have shown in particular that the initial differences between cells are maintained at all temperatures to an order of accuracy approaching 1 part in 100,000. The true test of the reliability of a cell is the behavior of individual cells rather than the mean value of a large number. Initial differences do not seem to be so well preserved in the case of the Weston cell as for the Clark over an extended period, although it may yet be shown that the two are equal in this re-

spect. There can be no question, as to the superiority of the Weston cell as a working standard, quite apart from its value in accurate physical investigation, and its general adoption can be only a question of time.

All forms of the Clark cell, containing a saturated solution, have the same temperature coefficient, the only type possessing a different one being the Carhart-Clark with dilute solution.

In the case of the Weston cell it seems that four coefficients are possible, depending on the state of the cadmium sulphate solution. In a previous paper by one<sup>1</sup> of us it was pointed out that the type of cell known and described as the inverted cell<sup>2</sup> appeared to possess a greater temperature change than the cells made and tested at the Reichsanstalt by Jaeger and Wachsmuth.<sup>3</sup> At the same time one of the cells tested at that time, known as Cd H, was made after the pattern of Jaeger's cells. This cell, we found, possessed practically the same coefficient as the inverted. A 14.7 percent amalgam was used for all these cells, and made from some cadmium rod which had been in the laboratory some time previously. When tested qualitatively this cadmium was found free from zinc.

In these first tests great irregularity was shown below 15° C, and in some cases a sudden change in E. M. F. seemed to indicate a change in the hydration of the cadmium sulphate in a way similar to the change observed by Callendar and Barnes<sup>4</sup> for the Clark cell at 39°.

As originally stated, these first cells were made in order to verify the value of the Clark cell upon which the absolute value of the mechanical equivalent of heat measured by electrical means,<sup>5</sup> was based. As a matter of interest, however, the temperature change was determined and found larger than that ob-

<sup>1</sup> Jour. Phys. Chem. 4, 339 (1900).

<sup>2</sup> B. A. Report, Toronto, 1897, and the Electrician, 39, 68 (1897); 40, 165 (1897).

<sup>3</sup> Wied. Ann. 59, 575 (1896).

<sup>4</sup> Proc. Roy. Soc. 62, 148 (1897).

<sup>5</sup> Phil. Trans. A199, 149 (1902).

tained by Jaeger and Wachsmuth. It was not at all clear at that time why there should be such a large divergence in the results, for the only striking difference between our cells and those of Jaeger and Wachsmuth was in the use, both in the inverted and in the H-cell, of a mass of moist cadmium sulphate crystals in place of the saturated solution and crystals. The moist crystals were used on account of the great success attending the use of the same in the Clark "Crystal" cell.

Quite recently a large number of tests have been made by Jaeger and Lindeck<sup>1</sup> with both old and new Weston cells in order to verify the original temperature formula proposed by Jaeger and Wachsmuth.<sup>2</sup> These tests are very complete and show that for the cell with saturated solution as prepared in the Reichsanstalt, the temperature change of the E. M. F. may be accurately represented by the formula

$$E_t = E_{20} - 0.038(t - 20) - 0.00067(t - 20)^2,$$

expressed in millivolts.

The first term only need be considered unless working over a wide range of 10 or 20 degrees, and it may be stated that these cells possess an average change at ordinary temperatures of 0.0038 percent per degree. The temperature change observed for the inverted cells and H-cell with moist crystals and 14.7 percent amalgam amounted to 0.0086 percent per degree, which, as Jaeger points out, is double the other value.

In order to arrive at a satisfactory explanation of this matter further tests were made by one of us in 1901 with the assistance of Mr. H. Lester Cooke, M.A. A test-tube form of cell was constructed similar to the Clark "crystal" cell. This consisted, briefly, of a paste of mercurous sulphate and cadmium sulphate with amalgamated platinum cathode in the bottom of the tube, and a mass of moist crystals on top with an anode of cadmium amalgam cast in the form of a rod. The firmness of the cadmium amalgam made this possible. Two cells were made with a 14.7 percent amalgam, and seven others were made with a

<sup>1</sup> Zeit. für Instk. 21, 33 (1901); 21, 65 (1901).

<sup>2</sup> l. c.

13 percent amalgam. It had been shown by Jaeger that the use of the latter strength prevented the great irregularities observed below  $15^{\circ}$ . It was made clear by him also that the irregularities were due to the amalgam and not to a change in hydration of the sulphate. Moreover, he showed also that the solubility curve of the cadmium sulphate did not change below  $15^{\circ}$ , but that the curve was continuous.

While carrying out the tests on our new cells it was unfortunate that we were unable to verify the results for the original inverted cells, but all of these had to be abandoned on account of the separation of the crystals from the amalgam by a thin film of gas. To avoid this happening again the cadmium amalgam rod cell was devised, and the new cells made in the upright form.

The original inverted cells were made in 1897, but the tests on them were not published until 1900. The delay in publication resulted from our desire to find a satisfactory explanation of the wide divergence from the German values. Since, for other reasons, further delay was impossible, the results were published pending a more thorough investigation. The tests on these cells were carried out with the same apparatus used by Callendar and Barnes, and described fully in other places. It will not be necessary, therefore, to describe the measurements, since the method of procedure was the same as previously used.

We found that our cells showed considerable divergence as regards their temperature changes of E. M. F., and although our experiments were very carefully carried out and particular attention paid to the electrical readings, all our results were higher than the formula proposed by Jaeger and Wachsmuth. The cells were subjected to temperature changes between  $15^{\circ}$  and  $30^{\circ}$ , and  $15^{\circ}$  and  $0^{\circ}$ , ample time being allowed for the attainment of steady conditions. Large changes were observed at  $0^{\circ}$  in the cells containing the 14.7 percent amalgam, and much steadier and more consistent results were obtained with the other cells.

The changes in E. M. F., which we observed, varied between 0.0079 percent per degree for the cells with the 14.7 per-

cent amalgam to 0.0054 percent per degree for the 13 percent amalgam, between the intervals of temperature  $10^{\circ}$  and  $28^{\circ}$  C. Our tests were unsatisfactory in so far as they offered us no explanation of our higher values. They showed us, however, that the cells with 14.7 percent amalgam gave a distinctly higher change than the other cells. Unfortunately, owing to the stress of other work, we were obliged to abandon any further attempts at this time.

Recently a number of tests have been carried out by us on various types of cells, which shows us that the divergence in the temperature coefficient is really due to the strength of the cadmium sulphate solution.

Four cells were constructed in the inverted form with the purest possible materials. New cadmium metal was used for the amalgam, which was the best supplied by Merck. Moist crystals of cadmium sulphate were used as before, and our cells differed from the original inverted cells only in having a 13 percent amalgam made from different cadmium metal. One of our new cells was made in the H-form with a saturated solution in place of the moist crystals. Two of the cadmium rod cells tested in 1901 were also included, and in addition two cells supplied by the Weston Electrical Instrument Co. were subjected to temperature changes. These cells were lent to us by the Department of Electrical Engineering through the kindness of the director, Professor R. B. Owens, D.Sc. Jaeger and Lindeck have shown that these cells, with solution saturated at  $0^{\circ}$  and therefore unsaturated at ordinary temperatures, have a very small temperature coefficient, which changes sign at about  $20^{\circ}$ . A maximum value of the E. M. F. occurs at about this temperature.

We, therefore, had three types of cells; six cells with moist crystals which ensured saturation of the adhering liquid at all temperatures; a cell with solution saturated at  $20^{\circ}$  and no excess of crystals; and two cells with unsaturated solution.

We were unable to use the various pieces of apparatus hitherto employed for standard cell work in this laboratory,

owing to their use in other investigations, but another arrangement was quite as accurate and reliable, although not so convenient. For a thermostat we had a large copper air-bath with double walls through which water could be circulated at different temperatures. Some of the cells were not suited for direct insertion in a water-bath, so that the present arrangement was really better than our former one. All of the cells were placed in this bath and connections made with the outside by means of carefully insulated wires leading to a paraffin block with mercury cup contacts.

The electrical readings were made on the Kelvin-Varley slide potentiometer used and described in previous investigations in this laboratory. The errors of the various coils were all less than 1 part in 10,000, and determinations of the errors agreed in all cases for the 101 coils to a tenth of this amount. The resistance of the whole potentiometer was 100,000 ohms, and for reading the deflections with the vernier dial a Kelvin 100,000 ohm galvanometer was used. Our readings were in all cases accurate to 1 part in 50,000 at least.

Four Clark cells, kept in a water-bath, were read at the same time, and the values of our Weston cells were obtained in terms of them. Our method of measurement had the disadvantage of not being one of difference as formerly employed, but it had the advantage of direct comparison with the Clark cell without altering any connections.

Our first set of readings did not include the H-cell, this cell being made specially for and included in a second set of readings undertaken solely to compare the various temperature coefficients.

The following readings were obtained in comparing the Westons with the Clarks:

Of the Weston cells, Nos. 224 and 185 are the Weston Instrument Co.'s cells,  $Cd_{11}$  is one of the cadmium rod cells, and  $Cd_{16}$ ,  $Cd_{17}$ ,  $Cd_{18}$ ,  $Cd_{19}$  are the new inverted cells.

In regard to the Clark cells,  $X_2$  is one of the five original cells made in 1895 and still in the possession of the laboratory.  $X_{44}$ ,  $X_{45}$ ,  $X_{46}$  are three new cells which were made in 1901.



**WESTON CELLS**  
Temperature 19.9° C.

Cell	Pot. read.	Cell	Pot. read.
224	52993	Cd <sub>16</sub>	52995
185	53002	Cd <sub>17</sub>	52978
Cd <sub>11</sub>	53003	Cd <sub>18</sub>	52980
—	—	Cd <sub>19</sub>	52983

**CLARK CELLS**  
Temperature 14.96° C.

X <sub>2</sub>	X <sub>44</sub>	X <sub>45</sub>	X <sub>46</sub>
74517	74530	74530	74528

A similar comparison was made at two other temperatures, and the values referred to the Clark cells. The following readings were obtained :

**WESTON CELLS**  
Temperature 14.6° C.

Cell	Pot. read.	Cell	Pot. read.
224	53035	Cd <sub>16</sub>	53042
185	53040	Cd <sub>17</sub>	53028
—	—	Cd <sub>18</sub>	53030
—	—	Cd <sub>19</sub>	53033

**CLARK CELLS**  
Temperature 14.41° C.

X <sub>2</sub>	X <sub>44</sub>	X <sub>45</sub>	X <sub>46</sub>
74620	74630	74630	74630

A comparison of these three sets of readings will show that all of the inverted cells have the same coefficient for their relative differences are preserved throughout the range of temperature.

In working out the values of the cells we have taken for the Clark the value 1.43325 volts at 15° C, and corrected for

temperature by the formula  $E_T - E_{15} = -1.20(t - 15) - 0.0062(t - 15)^2$ , expressed in millivolts. This gives for the Weston Instrument Co.'s cells the values :

WESTON CELLS  
Temperature 27.9° C.

Cell	Pot. read.	Cell	Pot. read.
224	53052	Cd <sub>16</sub>	53023
185	53057	Cd <sub>17</sub>	53015
—	—	Cd <sub>18</sub>	53015
—	—	Cd <sub>19</sub>	53022

CLARK CELLS  
Temperature 14.61° C.

X <sub>16</sub>
74647

The maximum value, about 20°, corresponds to the results obtained by Jaeger and Lindeck, who found

1.01914 at 14.6° C.  
1.01916 at 19.9° C.  
1.01907 at 27.9° C.  
  
1.01886 at 13.3° C.  
1.01884 at 16.2° C.  
1.01886 at 19.7° C.  
1.01883 at 29.9° C.

The difference here in the absolute value is of course due to the fact that the value of the Clark cell assumed by the German authorities and used for reduction, is somewhat lower. It is given by Jaeger and Lindeck as 1.43291 volts.

The cells with unsaturated solution are somewhat higher than those with saturated solution as Jaeger and Lindeck point out. According to our values at 19.9°, this difference amounts to 0.00027 volt, which is almost identical to the values 0.00021 at 19.7° and 0.00025 at 19.8°, taken from Table IV of Jaeger and Lindeck for their older cells.

The average change per degree for the inverted cell is

found to be 0.0051 percent, which is lower than the value found before for the inverted cells with the 14.7 percent amalgam, but still in excess of the value for Jaeger's cells. The value agrees, however, with the value 0.0054 percent, obtained for the cadmium rod cells with a 13 percent amalgam.

The exceedingly small coefficient of the Weston Instrument Co.'s cells, and the lower values we obtained for our cells with 13 percent amalgam led us to think that a cell with solution of constant strength saturated at ordinary temperatures, together with the 13 percent amalgam, would give us a coefficient less than the new inverted cells, and therefore more in agreement with the German values. Our H-cell was therefore constructed with this in view and the second set of readings obtained to compare the coefficients of all the types. The following table contains the reading :

Cell	Temp. 13.6° C.	Temp. 18.7° C.	Temp. 29.5° C.
224	54164	54003	54187
185	54170	54010	54194
Cd <sub>16</sub>	54152	53985	54130
Cd <sub>17</sub>	54158	53990	54136
Cd <sub>18</sub>	54164	53995	54144
Cd <sub>19</sub>	54154	53987	54134
H-cell	54156	53995	54152
Cd-rod <sub>8</sub>	54192	53997	54142
Cd-rod <sub>11</sub>	54194	54015	54174

The following are the mean values for the different cells :

Cell	13.6°	18.7°	29.5°
Weston	54167	54007	54191
Inverted	54157	53989	54136
H-cell	54156	53995	54152
Cd-rod	54193	54006	54158

In working out the temperature coefficient of the cells the value of the Weston cell for each of the three temperatures is

taken by the comparison with the Clark and quoted from the previous tests. This was found necessary owing to the gradual change in the accumulator supplying the steady current to the potentiometer over the length of time, three days, occupied in taking readings. Six to eight hours was allowed at each point for the cells in the air-bath to take up a steady temperature.

It is worthy of note that the relative differences of the four inverted cells are maintained very closely. This is less satisfactory for the cadmium rod cells, but these cells are older and made with the old and possibly less pure cadmium metal. In addition  $Cd_8$  possessed a 14.7 percent amalgam and  $Cd_{11}$  a 13 percent amalgam. They are both included in the mean for this type of cell, but it is seen that  $Cd_8$  has a larger temperature coefficient than  $Cd_{11}$ .

The average change between  $13^\circ$  and  $29^\circ$  from these observations is, for each type of cell, as follows :

Cell	Temperature change per degree. Percent
Weston Inst. Co.	Negligible
Inverted	0.0058
Cd rod	0.0076
H-cell	0.00388

It is evident from these results that the divergence between the crystal cell and the H-cell with saturated solution is real, and has to do with the strength of the solution remaining constant in the latter case. The agreement of our H-cell with the German cells, where an excess of solution is used, makes it appear probable that both these cells are similar. That is to say the solution probably remains of constant strength at all temperatures. The difficulty of preparing a saturated solution of cadmium sulphate is very great. The last traces of salt are dissolved with difficulty, and it is only after vigorous shaking for several hours that the solution can be made. Diffusion alone would result in the solution requiring an almost infinite time to become saturated. Even in the Clark cell with zinc sulphate, which is much less difficult to prepare,

it has been shown that a period of two weeks was required for diffusion to take place on a change in temperature in one of the old forms of Board of Trade cell. In both our inverted and cadmium rod cells with the moist crystals the adhering solution is always saturated.

From the results of our experiments it is evident that cells with solution saturated at  $0^{\circ}$  have practically no temperature coefficient; that cells with a saturated solution of constant strength have a temperature change of 0.0038 percent per degree, that cells with moist crystals and a 13 percent amalgam have a temperature change of 0.0055 percent, and that cells with moist crystals with a 14.7 percent amalgam have a temperature change of 0.008 percent per degree.

#### **Ratio of Clark to Weston**

The ratio of our Clarks to our first Weston cells in the inverted form and with the 14.7 percent amalgam was found to be 1.40658. This value is a little lower than the latest values given for the cells in the possession of the Reichsanstalt, which makes it appear, in light of our recent work, that the inverted cells were too high. From the agreement of all the various types of Clark cells which we have made from time to time in this laboratory it is exceedingly unlikely that they are too low.

It is possible to obtain another value of the ratio from our new cells by the observations given in our first table.

If we take the mean of the four inverted cells at  $19.9^{\circ}$  C, which is in practical agreement with the H-cell, and compare this with the three new Clark cells,  $X_{44}$ ,  $X_{45}$ ,  $X_{46}$ , we obtain the value

$$\frac{\text{Clark at } 15^{\circ}}{\text{Weston at } 20^{\circ}} = 1.40666,$$

after applying the small corrections for the potentiometer.

Cell  $X_2$ , as before stated, is one of the five original "crystal" cells described fully by one of us, and used previously to obtain the ratio. It was found that this cell, as well as the other four, were a little too low when compared with all the other cells that were made at different times, which brought our original ratio

from 1.40644 to 1.40658.<sup>1</sup> Comparing the observations in our first table,  $X_2$  is seen to be a little lower than the new cells by almost exactly the same amount as was previously found, for this reason we have omitted it from the mean in the present determination of the ratio. The mean value of the ratio obtained at the Reichsanstalt is given by Jaeger and Lindeck<sup>2</sup> as 1.40665, which is coincident with our value.

We find it probable from a number of considerations that our original inverted cells were a little too high. Our cadmium rod cells, which were made with the first cadmium metal, are also a little high when compared with the new cells.

In conclusion we may remark that it is a matter of small moment which cell, the Clark or the Weston, is adopted as an official standard, since the ratio of the one to the other is known so closely. Both cells have points to recommend them for different types of work, but it is evident that the Clark cell will retire more completely into the laboratory as time goes on, leaving to the Weston cell the more active part of a general working standard.

*McGill University,  
Jan. 2, 1904*

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<sup>1</sup> See Phil. Trans. 199A, 149 (1902), for full history of these cells.

<sup>2</sup> Loc. cit.

# THE ACTION OF SODIUM AMALGAM ON SOLUTIONS OF POTASSIUM SALTS, AND OF POTASSIUM AMALGAM ON SOLUTIONS OF SODIUM SALTS

BY G. MCP. SMITH

In a thesis carried out by Gustave Fernekes at the University of Wisconsin, under the direction of Prof. Kahlenberg, and published in the December number of the Journal of Physical Chemistry, the following statements are made :

"It would seem that the action of the sodium and potassium amalgams on solutions of sodium and potassium salts should be fully accounted for by the ionic theory of Arrhenius. As stated above, this investigator attributed the slow action of sodium amalgam, for example, on solutions of sodium salts to ions of sodium in solution, which by mass action would prevent the entrance of more sodium ions into the solution. Although this theory is very plausible in the case of solutions of sodium salts with sodium amalgam, it fails to explain the slow action of the same amalgam on solutions of potassium salts. It is just as difficult to explain the slow action of potassium amalgam on solutions of sodium salts by this theory. . . . Numerous examples of the untenability of the ionic theory have been found since its establishment in 1887, and it is especially the series of investigations which have been carried out in this laboratory for a number of years under the direction of Prof. Kahlenberg, which show conclusively that this theory has outlived its usefulness. Prof. Kahlenberg has also been the first to suggest a new theory, which not only explains satisfactorily the facts whose interpretation required the complicated ionic theory, but which also throws light on the whole subject of solutions, explaining the facts whose interpretation by the old theory was difficult or absolutely impossible.

"Chemical affinity, the affinity between solvent and dis-

solved substance, and the formation of a true chemical compound whose properties are different from either constituent, form the basis of this new theory. It will be seen how simple the interpretation of the behavior of the amalgam on the different solutions is.

"To begin with, the solutions of the sodium and potassium salts of inorganic acids, whose action on the amalgams could not be explained by the ionic theory, will show how well the new theory applies. A solution of sodium chloride should retard the action of the sodium amalgam according to the ionic theory, because sodium ions in the solution will tend to prevent the entrance of more sodium in the ionic state. On the other hands a solution of potassium chloride should not retard the action of the sodium amalgam. The potassium ions can offer no resistance to the entrance of sodium ions. A glance at Figs. 1 and 2 will however show that potassium chloride retards the action, and furthermore that a normal potassium chloride solution retards about as much as a normal solution of sodium chloride. Prof. Kahlenberg's theory satisfactorily explains this by assuming that potassium chloride has about the same affinity for water as has sodium chloride, on account of the similarity of the two salts. The water would in each case be held with the same degree of tenacity, and the action of the sodium on the new compound would in each case suffer an equal retardation. The same explanation of course holds in the case of potassium and sodium salts in general if we compare isotonic solutions of these salts. The theory also accounts for the same phenomenon observed with potassium amalgam. . . . A new chemical compound then is formed between the water and the salt which, if similar, will also have similar action on the respective amalgams."

Upon reading the above statements, it occurred to me that the action referred to could be much more plausibly explained by the ionic theory of Arrhenius than by the hypothesis of Prof. Kahlenberg, as follows :

The solution of the potassium salt, containing positively charged potassium ions, brings about the replacement of a part



of the sodium in the amalgam by potassium in the following manner: The positive charge of a potassium ion is neutralized by the negative electricity of a neutral sodium atom (containing

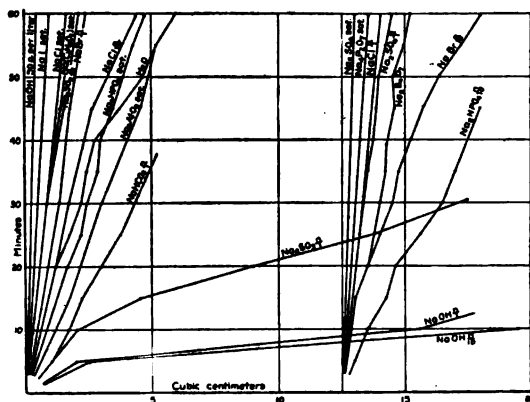


Fig. 1

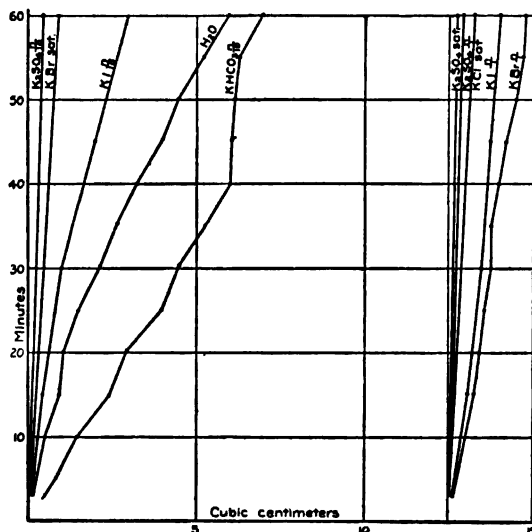


Fig. 2

both positive and negative electricity) upon coming in contact with the latter, and thus leaves the sodium atom positively charged, i. e., an ion; the potassium atom entering into the amalgam and the sodium ion into the solution. How much

sodium is thus replaced, depends upon the conditions under which the experiment is carried out.

If a relatively large number of potassium ions are in the solution, as compared with the number of sodium atoms in the amalgam, the sodium of the amalgam is according to the law of mass action almost entirely replaced by potassium, and, after this has happened, the potassium (and the remainder of the sodium) in the amalgam is free to act on the solution, which now contains both potassium and sodium ions. This accounts in a very satisfactory manner, for example, for the slow action of sodium amalgam on a solution of potassium chloride. At the beginning, the main process consists in the replacement of sodium by potassium, and, as soon as an equilibrium has been approached in this direction, the resulting amalgam is free to act on the water of the solution with the evolution of hydrogen, and the formation of potassium (and sodium) hydroxide. It is now easy to see why this action is retarded. The sodium and potassium ions of the solution tend to prevent the entrance of more sodium and potassium in the ionic state.

In the same way, the slow action of potassium amalgam on solutions of sodium salts is explained, a part of the potassium of the amalgam being replaced by sodium, according to the law of mass action.

In order to test the accuracy of the above reasoning, the following experiments were performed :

About 50 grams of clean sodium amalgam, containing approximately 1 percent of sodium, was covered in a small beaker with a layer of saturated potassium chloride solution about one inch in thickness, and allowed to stand for 15 minutes at the ordinary temperature. The solution was then poured off, the last traces absorbed with filter-paper, and the amalgam thoroughly washed with water. The amalgam, which was now of a more crystalline nature, though it contained enough mercury to remain still liquid, was covered with distilled water, and heated on a water-bath until the evolution of hydrogen ceased. The resulting solution was decanted, neutralized with hydrochloric acid, and platinum chloride added in slight excess,

together with a little alcohol. Hereby enough potassium platinum chloride was precipitated to cover the bottom of a small beaker with a layer of about 1 mm in thickness. The precipitate was filtered off, washed with 90 percent alcohol, and tested in a Bunsen flame on platinum wire. It gave a beautiful potassium flame.

An analogous experiment was made with potassium amalgam and sodium chloride solution, with a like result.

The potassium amalgam was prepared by warming 130 grams mercury in a porcelain dish, covering its surface with petroleum, and adding 1.1 grams potassium in small portions. This amalgam, after having been cleaned, contained approximately 1 gram of potassium. It was allowed to stand in a small beaker for 30 minutes under a saturated solution of sodium chloride. The solution was then poured off and tested for potassium, of which a considerable quantity was present in it. The amalgam was dried by means of filter-paper, and then thoroughly washed with water. It was then covered with water and heated on a water-bath as long as hydrogen continued to be evolved. The resulting solution was acidified with hydrochloric acid and evaporated to dryness. The residue was taken up in as little water as possible, filtered into a test-tube, and dry hydrochloric acid gas passed over the surface of the liquid until a saturated solution was obtained. In this manner the sodium was practically all precipitated as sodium chloride. A very small quantity of water ( $\frac{1}{2}$  cc) was now added, and the contents of the test-tube well stirred with a glass rod. Then the sodium chloride was filtered off and washed four times with 95 percent alcohol. The filtrate contained very little potassium, but the precipitate of NaCl weighed, after drying at  $110^{\circ}$ , 1.25 grams—i. e., at least 0.83 gram potassium, out of a total of not more than 1.1 grams, was replaced in the course of 30 minutes by sodium.

At this point, I thought it would be well to look up the literature on amalgams, in order to see if anything had already been done along these lines, besides the preparation of ammonium amalgam. I was very much surprised to find, under one of the references cited in the above publication,<sup>1</sup> that other amalgams had been prepared by this method.

<sup>1</sup> Wied. Ann. 43, 101-125 (1891).

The article cited is an "Inaugural Dissertation," by J. Schumann, carried out under the direction of Prof. Wiedemann at Bamberg. Among other things he says:

"Um Baryumamalgam zu erhalten, habe ich 1 Proz. Natriumamalgam in eine erhitzte Chlorbaryumlösung gebracht. Das so gewonne Amalgam," etc.

"Ausserdem erhielt ich Kaliumamalgam durch Einbringen von Natriumamalgam in Kalilauge, wobei die Alkalimetalle nach längerer Zeit ihre Stellen auswechseln."

Besides these he prepared in this manner amalgams of cobalt, copper, magnesium, manganese, etc., and under sodium amalgam he says: "1 Proc. Natriumamalgam zersetzt die Chloride der meisten Metalle und bildet mit den letzteren Amalgame." He also prepared nickel amalgam from zinc amalgam and  $\text{NiCl}_2$  solution.

That this method is not new is shown by the fact that at the beginning of his dissertation Schumann says he prepared his amalgams mostly after methods given in the hand-books of Gmelin-Kraut, and Graham-Otto; and in the latter work I found that barium amalgam had been prepared by the action of sodium amalgam on barium chloride solution at least as early as 1862.<sup>1</sup>

But nowhere have I seen that sodium amalgam has been prepared from potassium amalgam, or from magnesium amalgam, etc., as should also be possible according to the ionic theory and the law of mass action.

The preparation of an amalgam containing sodium, from potassium amalgam, has been given above. By treating potassium amalgam (or others) successively with fresh portions of a saturated solution of sodium chloride, for example, it should be possible to replace all the potassium (or other metal) by sodium in the course of a short time.

Further work along this line will be presented in a subsequent paper.

*Michigan College of Mines,  
February, 1904.*

<sup>1</sup> Jahrestber. Chem. 1862, 126.

## NEW BOOKS

*Diagrammes et Surfaces thermodynamiques.* By J. W. Gibbs. *Scientia*, No. 22. 13 × 20 cm; pp. 86. Paris: C. Naud, 1903. Price: 2 francs. — This number of the *Scientia* series is a French translation of Gibbs's two papers, on graphical methods of thermodynamics, from the second volume of the Transactions of the Connecticut Academy. It is prefaced by a fourteen-page introduction, a brief biographical note, and a bibliography of Gibbs's publications. The interesting and appreciative introduction, by Professor B. Brunhes, of the University of Clermont, is in the main a geometric study of the mutual relations of the energy, free energy, heat function, and thermodynamic potential surfaces. Because of the relative inaccessibility of the original papers, the little book will be of material service to students of thermodynamics everywhere.

J. E. Trevor

*Thermodynamics and Chemistry, a non-mathematical treatise for chemists and students of chemistry.* By P. Duhem. Authorized translation by George K. Burgess. 15 × 23 cm; pp. xxi + 441. New York: John Wiley and Sons, 1903. Price: bound, \$4.60, net. — We take pleasure in calling attention to the appearance of an English translation of Duhem's beautiful little non-mathematical work on thermodynamics, written for the use of students of chemistry. Since the original edition of the book was fully reviewed in this Journal (6, 193) on its appearance, it is not necessary to examine it with detail now. Let it suffice to quote, from the author's introduction to the edition, the following passages: —

"I am glad, in the first place, to have my treatise rendered easily accessible to American students; one of the objects which I had in mind when writing it was to make the work of J. Willard Gibbs known and admired; I like to think it will contribute to enhance, within your active universities, the glory of your illustrious countryman.

"Furthermore, this glory is more and more resplendent every day; more and more clearly the author of the *phase law* appears as the initiator of a chemical revolution; and many do not hesitate to compare the Yale college professor to our Lavoisier.

"Chemists had fixed upon a certain number of properties by which they recognized a substance to be a definite compound; these characteristics are effaced by the *phase rule*; many substances, to which formulæ had been attributed, are erased from the number of combinations; chemical science as a whole needs a revision at which the laboratories of America and Europe are working most diligently.

"Nevertheless, whatever be the outcome of this revolution, it seems to me there is injustice in making the glory of Gibbs consist in this alone, by seeing in him merely the author of the phase rule. In his immortal work, *On the Equilibrium of Heterogeneous Substances*, this rule is not all; it is but one

theorem, and is accompanied by other propositions whose importance is not less; the theorems on indifferent points, the laws of dissociation of perfect gases, the properties of dilute solutions, the conditions of osmotic equilibrium, the theory of the voltaic cell, bear, not less than the phase rule, the mark of the genius of their author." . . .

"At the start the wholly algebraic doctrine of Gibbs did not find in the country of its creator experimentalists to transform it into chemical theory; it first found them in Holland. From this again, it seems to me, we may learn a lesson. The full discovery of the truth requires the concurrence of all peoples, their diverse intellectual aptitudes, their different ways of conceiving an idea, of developing it, and of expressing it. In this respect, exclusiveness would again be punished by sterility.

"You agree with this, for you have judged it useful to mitigate the vigorous and assertive initiative which the American universities impart to their students by the discipline of equilibrium and of proportion which French teaching imposes; what you have tried in your own intellectual formation you wished to procure for others; you have desired to make known to your countrymen the book in which I have tried to expose, with French neutrality, ideas coming from America; I could not wish an interpreter better prepared to diffuse my thought."

J. E. Trevor

*Treatise on Thermodynamics. By Max Planck. Translated by Alexander Ogg. 14 X 22 cm; pp. xii + 272. New York: Longmans, Green, and Co., 1903. Price: bound, \$3.00.* — The popularity of Planck's treatise on thermodynamics undoubtedly justifies the issue of this very well made English translation of it. The book begins with a discussion of the ideas of temperature, molecular weight, and quantity of heat, passes to development of the first and second laws of thermodynamics, and concludes with applications of the thermodynamic principles to homogeneous systems, systems in different states of aggregation, systems of any number of independent components, gaseous systems, and dilute solutions.

Despite its many admirable features, the treatment is open to several serious objections. One relates to the employment of Planck's fundamental function, which is the Massieu-Gibbs thermodynamic potential divided by the absolute temperature and taken negatively. The properties of this function are not as simple as are those of any one of the Gibbsian fundamental functions. Other obvious objections have been so well stated in a recent review (*Nature*, Dec. 31, 1903) of this work that they are reproduced here.

"The method of introducing such notions as temperature and entropy cannot be regarded as satisfactory. We find in chapter I. the usual juggling with the terms "perfect gas" and "absolute temperature." Thus absolute temperature is defined in § 9 by the expansion of gases, while in § 24 these gases are shown to obey laws which are not rigorously consistent with this definition of temperature. The term "perfect gas" is introduced in a vague sort of way in this chapter, but without sufficiently definite statements being made as to what is a perfect gas and what is not. To define absolute temperature by means of a perfect gas and then define a perfect gas by means of its laws of expansion referred to absolute temperature is merely working round in a circle.

Moreover, the *entropy* of unit mass of a substance is defined, in the first instance, by the formula

$$\phi = c_v \log \theta + R/m \log v + \text{const.},$$

applicable to the case of a perfect gas. . . . "To define a physical quantity in the first instance by means of its value in a particular case, when the definition is not valid in the more general case, is certain to be misleading, and no amount of subsequent discussion, such as Prof. Planck admittedly gives, can set matters right."

Apart from objections of this sort, the author's work has been uncommonly well done. It is the plan of the treatment, rather than the execution in detail, that arouses criticism.

J. E. Trevor

**Physical Chemistry for Physicians and Biologists.** By Ernst Cohen. Authorized Translation from the German by Martin H. Fischer. 13 × 19 cm; pp. viii + 343. New York: Henry Holt and Company, 1903. — This book having been appreciatively noticed at length in this Journal (5, 657) on its first appearance, there remains now only to chronicle with pleasure the appearance of an English translation of it. The version reads smoothly, and has evidently been prepared with care. An unfortunate oversight is the omission of a table of contents. Suitable indices are, however, not lacking.

J. E. Trevor

**A Text-book of Organic Chemistry.** By A. F. Holleman. Translated by A. Jamieson Walker, assisted by Owen E. Mott, with the co-operation of the author. 15 × 23 cm; pp. xvii + 555. New York: John Wiley and Sons, 1903. Price: bound, \$2.50. — Those who are familiar with Prof. Holleman's excellent text-book of inorganic chemistry will have no reason to be disappointed in the present, companion volume, for the text of this work shows the same broad and thorough knowledge as the former, and the same desire to infuse into this study something of a modern feeling.

The opening chapters deal with such subjects as analytical methods, molecular weight determinations, separation by distillation, — including a brief discussion of the vapor pressures of liquid mixtures, — determinations of boiling-point, melting-point, etc., passing on then to the consideration of the different classes of saturated compounds, — hydrocarbons, alcohols, (introducing stereoisomerism with the amyl alcohols), alkyl monohalides, esters, ethers, sulphur compounds, nitrogen compounds, on to acids, aldehydes, and ketones. Then follow the unsaturated compounds of the fatty series, and their derivatives; then "compounds containing more than one substituting group", — alkyl polyhalides, polyhydric alcohols; then polybasic acids, including an excellent treatment of the isomerism of fumaric and maleic acids. The subject of tautomerism, the oxonium compounds derived from di-methylpyrone, urea, uric acid, all these and many other topics come in later for clear, though brief consideration, and this part of the work ends with a chapter on the polymethylene derivatives.

The second part is given up to the aromatic series, and benzene and its derivatives are there treated in somewhat the same order that is observed in the first part. A final section deals with the albumins.

In a work so good as this it is no pleasure to call attention to small faults, yet the use of *ba* on p. 37 and elsewhere as signifying  $\frac{1}{2}Ba$  in an equation shall not go unnoticed; and there are here and there slight misprints.

As a whole, the book can be commended in the highest terms, and the translators are to be congratulated on having rendered it into very readable English. The print is plain if not fine.

A. P. Saunders

**Light Waves and their Uses.** By A. A. Michelson. *The Decennial Publications of the University of Chicago, Second Series, Volume III.* 15 × 22 cm; pp. 166. Chicago: The University of Chicago Press, 1903. Price: bound, \$1.50, net. — This book reproduces a course of lectures delivered before the Lowell Institute in 1899. After a general discussion of waves, in which it is shown that their most important characteristic is their ability to produce interference phenomena, the lectures deal with the employment of interference in the production of a natural standard of length, in the analysis of the vibrations emitted by a source of light, and in the measurement of very small distances and angles. Being a first-hand account of Michelson's own researches, and presented in a form adapted to a general audience, it will not fail to fascinate anyone who is at all interested in physical science. J. E. Trevor

**Introduction to the Rarer Elements.** By Philip E. Browning. 15 × 23 cm; pp. viii + 157. New York: John Wiley and Sons; London: Chapman and Hall, 1903. Price: cloth, \$1.50, net. — The author discusses each of the rarer elements in detail, giving consideration to the discovery, occurrence, extraction, preparation, and properties of the several substances. A list of typical compounds and their leading characteristics, together with a description of the best methods for the determination and separation of the rarer elements, and a list of laboratory experiments to be performed with each group are also included.

The author is to be congratulated upon the clear and interesting manner in which he has presented this most complex subject. The book will form a very useful and valuable guide to those who are interested in this branch of inorganic chemistry and to such analysts as have to deal with the separation and determination of these elements.

It is to be regretted that the details under some of the methods for the separation and purification of the rarer elements are so meagre, and it is to be hoped that in a second edition these may be considerably expanded.

A few inaccuracies have crept into the first edition. Thus, on page 33, it is stated that cerous salts may be oxidized by means of hydrogen dioxide. Under suitable conditions this substance is also one of the most efficient reducing agents for changing ceric salts to cerous compounds. In the same paragraph it is stated that solutions of pure cerium salts give no absorption spectra. The word spectra should be "bands." On page 35 the substance  $KN_3$  is called potassium nitride, a name that properly applies to the compound,  $K_3N$ . On page 40 it is stated that didymium may be separated into praseodymium and neodymium by the fractional crystallization of the double ammonium nitrates, whereas it is almost impossible to effect this separation if only these two elements are present. On page 42 the precipitate of cerium obtained by the addi-



tion of ammonium hydroxide and hydrogen dioxide is said to be of an orange-yellow color. On the contrary, this substance resembles ferric hydroxide very closely. Under the directions given for the extraction of thorium from monazite, we are told that thorium oxalate, after solution in ammonium oxalate, is separated by cooling the solution, filtering, and adding hydrochloric acid to the filtrate. But unless the solution is also diluted before filtration, some of the oxalates of the other rare earths will remain in the solution and be precipitated with the thorium oxalate. Among the omissions in the work might be mentioned the method of Muthmann for the separation of cerium, and that of Staudenmeier for the separation of tellurium and the preparation of pure telluric acid. These points, however, are of but minor importance and do not seriously impair the value of this most useful and interesting work. *L. M. Dennis*

**Quantitative Chemical Analysis.** By C. Remigius Fresenius. *Authorized Translation of the Greatly Amplified and Revised Sixth German Edition, by Alfred I. Cohn. 15 × 23 cm. Vol. I, pp. xii + 780; Vol. II, pp. xxii + 1255. New York: John Wiley and Sons, 1904. Price: both volumes, \$12.50.*—Everybody knows the work of the deceased master analyst. Analytical methods keep pace with chemical thought. The latter surges these days and is ever dependent upon the former. The users of the fifth edition soon learned the need of inter-leaving. The author incorporated such in the sixth edition. Two thoughts came to the reviewer. First, when are books of this character to be made according to the separate sheet system? Second, science is lauded as knowing no national limitations, when are we to remove the linguistic boundary lines? Utopian perhaps, for an American, the dream of an uniform language when we haven't even an uniform system of measurement!

The rendering of this standard text has been doubly well done by the translator, inasmuch as he omitted some of the antiquated methods and incorporated some of the more modern ones. We rather incline to the opinion it would have been well to use the blue pencil even more rigorously, vide, the old charcoal trough of Liebig for heating tubes. Unfortunately some of the late approved methods and apparatus are not given, as the Shimer crucible for carbon, electric heating oven, ammonium persulphate determination of manganese, estimation of chromium by sodium dioxide fusion, and so on. Yet Gooch's revolving cathode apparatus for copper is seen.

The translator recalculated all the values in the original book on the basis of the table of atomic weights reported in 1902.

The excellent methods of the Association of Official Agricultural Chemists and Hillebrand's elegant "Principles of Rock Analysis" are bodily reprinted as two appendices. This Journal limits the reviewer. Perhaps it is just as well, for some of these matters are of opinion. Also, perhaps a sufficiently liberal discount is allowed the purchaser in view of the fact that one-tenth of the two volumes may be had for the asking at Washington.

The typography is good on the whole. One does not expect blemishes in a big work like this, and dislikes meeting with even the few errors. The elegance of the book is injured by some sixteen pages of advertising matter in the rear. Each volume has a useful index. *Chas. Baskerville*

**Elementary Chemistry.** By Robert Hart Bradbury. 14 X 20 cm; 392 pp. xii + 329. New York: D. Appleton and Company, 1903. — The headings of the earlier chapters of this book, taken in order, are:—Water; Solution; Physical and chemical change; Mixture—Element—Compound; Hydrogen; Oxygen and hydrogen peroxide; Combustion; Naming chemical compounds—Chemical symbols and equations—Different kinds of chemical change; Salt and sodium; Chlorine; The chlorides—Compounds of chlorine containing oxygen; The atomic theory—The law of multiple proportions; The atmosphere—Nitrogen; Compounds of nitrogen and hydrogen; Compounds containing nitrogen and oxygen; Atomic and molecular weights—Avogadro's law; Acids, bases, and salts—Electrolytic dissociation—Metals and non-metals. This brings us to page 135, and from this point onwards the author considers the elements by groups, beginning with the sodium group and passing on to a consideration of all the commoner elements, but without introducing the periodic system until the second last chapter.

It has seemed worth while to give the arrangement of the text thus fully because in this respect the work offers something new in the treatment of the subject. It represents an attempt to arrange the material in a more rational and more natural sequence than the conventional one, and the result should be a lessening in the difficulties which beset the student in the first few months of chemical study. The reviewer has for years followed a somewhat similar plan, and believes that it has advantages over the older one in which the student was introduced at once to something entirely unfamiliar, — either hydrogen or oxygen, — and was only afterwards led on to the study of so familiar a substance as water. It may well be questioned whether there is an advantage in putting off the consideration of Avogadro's hypothesis (here called Avogadro's law) so long as Dr. Bradbury does; or in setting the atomic theory before the law of multiple proportions; or in postponing the periodic system to the end of the book, and thus depriving the student of one of the best aids towards getting a general grasp of the subject. In fact there is much in the order of presentation, especially in the theoretical chapters, that invites discussion; so that the strength and weakness of the book alike may be found to lie in its arrangement of material.

In the selection of material as well the author has broken away somewhat from convention, and there is much matter here that fails to find a place even in larger texts; but while this has the advantage of adding variety and interest to the pages, it must be admitted that one often has the impression that this variety is gained at the cost of a thorough development of the more important lines of the subject; the chapters touch on too many different topics; they are at the same time too complete and too incomplete.

Taking it all in all, however, the book is much more of a contribution than most elementary texts, and it is commended to the attention of all who teach elementary chemistry; it is sure to be suggestive, if not always convincing.

A. P. Saunders

**Elementary Chemistry: Part II, Experimental Work.** By Robert Hart Bradbury. 14 X 20 cm; pp. viii + 155. New York: D. Appleton and Company, 1903. — The experiments included in this volume follow the same lines as the text noticed above. The directions are carefully worked out, and are evidently the result of laboratory experience and not merely written in the author's

study. The print of both volumes is very clear, and while the text is not free from errors, the reviewer has not noticed any important misprints.

A. P. Saunders

**Das Weltgesetz des kleinsten Kraftaufwandes in den Reichen der Natur. I. Band: In der Mathematik, Physik, und Chemie.** By *Gustav Portig*. 15 × 23 cm; pp. xii + 332. Stuttgart: Max Kiemann, 1903. Price: 8 marks.

**Die Grundzüge der monistischen und dualistischen Weltanschauung, unter Berücksichtigung des neuesten Standes der Naturwissenschaft.** By *Gustav Portig*. 15 × 23 cm; pp. ix + 105. Stuttgart: Max Kiemann, 1904. Price: paper, 2; bound, 3 marks.

Of these two books, written by a professional philosopher, the first is an endeavor to trace in mathematics, in physics, and in chemistry, the rôle of the inductively established principle that always and everywhere the greatest effect is associated with a minimum employment of force. The second, announced as a separately printed portion of the second volume of the treatise, is intended to serve as an introduction to the whole. The author states that his work is an attempt to develop a philosophy to which the results of mathematics, physics, and chemistry lead, and that "it is better that a philosopher should furnish this service of natural science than that a scientist should arouse the appearance of too great a claim upon fame."

J. E. Trevor

**Die Energie und ihre Formen.** By *A. Helfenstein*. 15 × 23 cm; pp. iv + 151. Leipzig und Wien: Franz Deuticke, 1903. Price: paper, 4.20 marks. — This is a long critical essay, the purpose of which is stated to be to assign to their proper places the axioms that support the existence of our material world. The present study is concerned with the "axiom of the conservation of energy." Subsequent publications are to deal with "the axiom of the conservation of masses, and the axiom of the conservation of space."

J. E. Trevor

**Zur Atombewegung, Kritik und Neues.** By *Johannes Hundhausen*. 13 × 19 cm; pp. 54. Leipzig: Johann Ambrosius Barth, 1903. Price: paper, 1.20 marks. — It is not very easy to see what this brochure is about. It may be that the author's difficulty and his solution of it are expressed by the following passages:

"The science of the present time does not possess a general unitary principle for the explanation of all motion-processes." . . . "Since form appears as resistance to motion, through which it itself has initially been produced, it must have a corresponding reaction upon this motion which leads it [the motion?] to the formation of like or similar forms."

These sentences may give the author's leading idea; the present writer hopes that they do.

J. E. Trevor

**Annuaire pour l'An 1904. Publié par le Bureau des Longitudes.** 10 × 15 cm. Paris: Gauthier-Villars. Price: paper, 1.50 francs. — The *Annuaire* of the Bureau of Longitudes for 1904 contains over seven hundred pages of its usual tabulations of astronomical, physical, and chemical data. The special features of the issue are a note, by M. Bouquet de la Grye, on the international geodesic conference held at Copenhagen in August, 1903, and an article by M. P. Hatt, giving an elementary explanation of the tides.

J. E. Trevor

## REVIEWS

*The object of this department of the Journal is to issue, as promptly as possible critical digests of all Journal articles that bear upon any phase of Physical Chemistry*

### General

**Revision of the atomic weight of lanthanum.** *B. Brauner and F. Pavlicek. Jour. Chem. Soc. 81, 1243 (1902).* — "All atomic weight determinations of the rare earth elements made by the synthetical sulphate method during the nineteenth century are vitiated by an error which tends to lower the atomic weight and diminishes as the basicity of the earth decreases." This is due to the lack of any satisfactory test to determine the point when one has the neutral sulphate. It would seem as though heating in a current of  $\text{SO}_3$  might be worth trying. The final result for lanthanum is 139.04; but this has since been the subject of discussion (7. 222, 307; 8. 62). *W. D. B.*

### One-Component Systems

**On the change of rock crystal into the amorphous state.** *M. Herschkowitsch. Zeit. phys. Chem. 46, 408 (1903).* — When rock crystal is to be converted into amorphous quartz, it should be heated slowly to  $570^\circ$  and then as rapidly as possible to the highest temperature. In this way cracks can be avoided. While some pieces of amorphous quartz have a milky look owing to microscopic cracks, this appearance is more likely to be due to a crystallization. This recrystallization practically does not take place at all at ordinary temperatures; but the change occurs with perceptible speed at  $1000^\circ$ . Amorphous quartz is not as permeable as the rock crystal for the shortest ultra-violet ray, less than  $193\mu$  for instance. As there is quite a difference between different plates of amorphous quartz, it is quite possible that this defect may be remedied some day. *W. D. B.*

**An accurate method of measuring the compressibilities of vapors.** *B. D. Steele. Jour. Chem. Soc. 81, 1076 (1902).* — Description of an apparatus for determining the pressure-temperature relations of vapor with reference to hydrogen and with an accuracy of one in three thousand. *W. D. B.*

**Atomic and molecular heats of fusion.** *P. W. Robertson. Jour. Chem. Soc. 81, 1233 (1902).* — "For the elements with atomic weights over 40 which do not expand on freezing, the expression  $Mw/T_f V$  gives numbers the derivation of which from the mean is but slightly greater than that observed in the case of Dulong and Petit's law.

"For the binary inorganic compounds, the mean percentage deviation of the values of  $Mw/T_f V$  is only  $\pm 5$ .

"In the case of the carbon compounds, great regularity is noticed among

those of similar constitution. Thus for the disubstituted benzenes the variation is  $\pm 5$  percent. Compounds with two benzene nuclei give equally satisfactory results."

W. D. B.

### Two-Component Systems

**Crystallization in binary systems.** *W. D. Bancroft. Zeit. phys. Chem.* 46, 87 (1903). — A discussion of the quantitative relations when a two-component melt is allowed to cool and the solid phase removed as fast as formed. It is pointed out that the same quantitative results are obtained if one assumes complete hysteresis in the solid phase. The more rapidly a casting is made the more closely will this state be reached, while an annealed casting will show the characteristics of a slowly-cooled melt from which the solid phase has not been removed.

W. D. B.

**The solubility curve of the hydrates of nickel sulphate.** *B. D. Steele and F. M. G. Johnson. Jour. Chem. Soc.* 85, 113 (1904). — The quadruple point with nickel sulphate heptahydrate and ice as solid phases occurs at  $-4.15^\circ$ ; the blue hexahydrate appears at  $+31.5^\circ$ , and the green hexahydrate at  $53.3^\circ$ . At some temperature above  $100^\circ$ , the green hexahydrate changes to the dihydrate. Solubility data were obtained from  $-4.15^\circ$  to  $+99^\circ$ .

W. D. B.

**The change of the melting-point of Glauber's salt with pressure.** *G. Tammann. Zeit. phys. Chem.* 46, 818 (1903). — The boundary curve for hydrated sodium sulphate, anhydrous sodium sulphate and melt passes through a maximum temperature.

W. D. B.

**On frost curves.** *W. Meyerhoffer. Zeit. phys. Chem.* 46, 379 (1903). — Starting with a two-component gaseous mixture, Duhem has called the pressures at which the first trace of liquid appears the dew curve and the pressures at which the last trace of vapor disappears the boiling curve. The author has discussed the corresponding cases for the equilibrium between vapor and solid instead of vapor and liquid. The "frost curve" corresponds to the dew curve and the sublimation curve for the boiling curve. A number of special possible cases are discussed in detail.

W. D. B.

**The solubility of mannitol, picric acid and anthracene.** *A. Findlay. Jour. Chem. Soc.* 81, 1217 (1902). — The author has made a few determinations on the solubility of mannitol and picric acid in water and of picric acid and anthracene in benzene. He then constructs the solubility curve by "comparison of a known solubility curve" (6, 431). The author is evidently not familiar with Kuriloff's work on benzene and picric acid, and he does not discover that the solid phase is benzene picrate.

W. D. B.

**The solubilities of some sparingly soluble salts.** *R. Abegg. Zeit. phys. Chem.* 46, 1 (1903). — Electrometric measurements were made with saturated solutions of silver chloride, bromide, sulphocyanate, oxide, carbonate, chromate and borate. In a table are given the solubilities of all sparingly soluble silver salts so far as these are known.

W. D. B.

**Solubility studies on sparingly soluble substances.** *W. Böttger. Zeit. phys. Chem.* 46, 521 (1903). — The author has determined carefully the electro-

lytic conductivity of saturated solutions of thirty salts of calcium, silver, thallium and lead. From these data he has calculated the solubilities. While great care has been taken in almost every way, the author has refrained deliberately from approaching the saturation point from both sides. In spite of assurances to the contrary, one feels that this has made it impossible for anybody to state what the accuracy of the measurements really is. *W. D. B.*

The molecular lowering of the freezing-point of water produced by concentrated solutions of certain electrolytes. *H. C. Jones and F. H. Getman. Zeit. phys. Chem.* **46**, 244 (1903). — The authors confirm the general results of Kahlenberg (5, 352–376), but explain the phenomena on the assumption of electrolytic dissociation plus hydration, the amount of hydration being that necessary to make the results conform with the theory. *W. D. B.*

Freezing-point and boiling-point experiments on molecular weight determinations. *E. Beckmann. Zeit. phys. Chem.* **46**, 853 (1903). — Methylene iodide has two freezing-points and the author has succeeded in making cryoscopic measurements with each modification. Molecular weights were obtained corresponding to  $S_8$ ,  $Se_{10}$ ,  $P_4$ , and  $I_2$ . In boiling bromine, molecular weights were obtained corresponding to the values  $Al_2Br_6$ ,  $SnBr_4$ ,  $SbBr_3$ , and  $AsBr_3$ . *W. D. B.*

The influence of temperature on association in benzene solution, and the value of the molecular rise of boiling-point for benzene at different temperatures. *W. R. Innes. Jour. Chem. Soc.* **81**, 682 (1902). — A number of boiling-point determinations were made under varying pressures with benzene as solvent. In most cases there was no evidence of a change of molecular weight with the temperature. The exceptions were benzoic acid, *o*-bromobenzoic acid,  $\beta$ -benzil monoxime, and ethyl dimethyl tartrate. The heats of dissociation of the first three of these exceptions were calculated and found to be of the same order of magnitude as those for some vapors—between 5,000 and 25,000 calories. *W. D. B.*

A simple form of Landsberger's apparatus for determining the boiling-points of solution. *E. B. Ludlam. Jour. Chem. Soc.* **81**, 1193 (1902). — The hole through which the vapor passes into the boiling solution is closed partially by a glass bead. There is no reflux arrangement. *W. D. B.*

On the "Regnault law" of Duhem. *J. v. Zawidski. Zeit. phys. Chem.* **46**, 21 (1903). — Starting from some experiments of Regnault, Duhem deduced the possibility of two liquids, which have different vapor pressures, giving solutions over a finite range of concentrations which should show a constant vapor pressure and identity of composition between the coexisting vapor and solution phases. It is now shown that there is no experimental evidence for any such case and that there is therefore no reason to assume its existence. *W. D. B.*

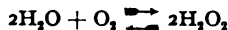
On critical temperatures of solutions. *M. Centnerzwer. Zeit. phys. Chem.* **46**, 427 (1903). — The critical temperatures were determined for solutions of a number of substances in ammonia and in sulphur dioxide. In each case the solute boiled at least  $100^\circ$  above the solvent and in each case the solution had a higher critical temperature than the solvent. The critical tempera-

ture was taken as the temperature at which the meniscus disappeared in the middle of the tube. The rise of critical temperature is practically proportional to the concentration of the solute and independent of its nature for moderately dilute solutions. W. D. B.

On the vapor pressure of solid solutions. *A. Speranski. Zeit. phys. Chem.* 46, 70 (1903). — Naphthalene has a vapor pressure of 7.4 mm Hg at 80°, while the vapor pressure of  $\beta$ -naphthol is very small at that temperature. With a modified Bremer-Frowein tensimeter, the author has measured the vapor pressures of solid solutions of  $\beta$ -naphthol in naphthalene. The pressures are lower than those of pure naphthalene at the same temperatures. Assuming the applicability of the van't Hoff-Raoult law, the author calculates molecular weights for  $\beta$ -naphthol of 198–255 instead of the value of 144 required by the formula. W. D. B.

The inclusion and occlusion of solvent by crystals. *T. W. Richards. Zeit. phys. Chem.* 46, 189 (1903). — The author gives his reasons for believing the errors due to inclusion and absorption are so great that it is "impossible to determine with the exactness demanded in the most accurate work the true weight of any salt containing water of crystallization". Even in the case of anhydrous salts or of metallic deposits it is by no means easy to drive off the last traces of included mother-liquor. Mechanical pulverization is not sufficient to break off all the hypothetical cells in which the mother-liquor is held. Fusion is effective and so is the crystallization of a volatile substance as solid solution. From the nature of the included solutions, a guess may be made at the conditions of formation of some minerals. W. D. B.

On the stability field for hydrogen peroxide. *W. Nernst. Zeit. phys. Chem.* 46, 720 (1903). — From potential measurements and from the heat of reaction, the author calculates that at 1260° the reversible reaction



will result in there being equal concentrations of water, oxygen and hydrogen peroxide under atmospheric pressure. At higher temperatures more hydrogen peroxide should be formed. Attempts to verify this conclusion failed utterly, but the author attributes this to a slow rate of reaction and not to any error in his reasoning. W. D. B.

The preparation of pure chlorine and its behavior towards hydrogen. *J. W. Mellor and E. J. Russell. Jour. Chem. Soc.* 81, 1272 (1902). — Pure chlorine was obtained by electrolyzing fused silver chloride between massive carbon electrodes. An electric spark causes an explosion in the dried, just as readily as in the moist mixture of hydrogen and chlorine. "Combination is complete, showing that the reaction is propagated through the whole mass of the gas. Neither heat nor sunshine causes explosion in the dried gases; combination, when it occurs at all, is very slow and incomplete, and not transmitted through the whole of the gas as in the previous case. Why there should be this difference, and whether the slow combination which we find is a direct action or due to a surface action, we are not at present in a position to say." W. D. B.

The union of hydrogen and chlorine, V. *J. W. Mellor. Jour. Chem. Soc.* 81, 1280 (1902). —

1. There is no experimental evidence to show that chlorine gas under the influence of light undergoes any change capable of appreciably affecting the chemical activity of that element towards hydrogen.

2. Part of the energy absorbed by moist chlorine from sunlight is dissipated as heat. This causes the Budde effect.

3. Under the influence of light, chlorine sets up and maintains in a state of equilibrium a reversible reaction with water vapor, possibly



4. Dry chlorine does not exhibit the Budde effect.

5. The rise in the temperature of imperfectly dried chlorine when exposed to sunlight appears to be due to some chemical reaction between the moisture and the chlorine gas.

6. A layer of moist chlorine just thick enough to screen a bulb of mixed hydrogen and chlorine gases from chemical action is not sufficient to prevent chemical action if the chlorine is dried by means of purified phosphoric oxide.

7. The actinic energy continuously absorbed from sunlight by moist chlorine is continuously dissipated in at least three ways: (i) partly in maintaining the above chemical action; (ii) partly by conversion into heat during molecular impacts; (iii) partly as external non-actinic radiations from the molecules moving in their free path between molecular collisions. *W. D. B.*

The union of hydrogen and chlorine, VI. *J. W. Mellor. Jour. Chem. Soc.* 81, 1292 (1902). —

"1. If the reaction between hydrogen and chlorine in the presence of moisture is assumed to take place with the formation of an intermediate compound, the period of induction is a direct consequence of the law of mass action.

"2. Since neither chlorine monoxide nor hydrogen hypochlorite abbreviates the period of induction, neither of these substances can take part, as intermediate compounds, in the reaction between hydrogen and chlorine.

"3. Since chlorine acquires no appreciable chemical activity by exposure to sunlight, the presence of hydrogen as well as of moisture determines the greater chemical activity of an induced mixture of hydrogen and chlorine gases.

"4. If an intermediate compound takes part in the reaction between hydrogen and chlorine in the presence of moisture, the most probable "compound" satisfying the required conditions contains  $x\text{Cl}_2$ ,  $y\text{H}_2\text{O}$ ,  $z\text{H}_2$ , where  $x$ ,  $y$ , and  $z$  are positive integers." *W. D. B.*

#### Multi-Component Systems

The solvent properties of mixed liquids in relation to the chemical characters and solvent properties of their components. *H. M. Dawson. Jour. Chem. Soc.* 81, 1086 (1902). — The distribution of iodine between an aqueous potassium iodide solution and a mixture of organic liquids cannot in general be calculated from the distribution coefficients for water and the organic solvents taken singly. The author believes that the variations are due to polymerization, for-



mation of compounds, etc. He cites the freezing-point experiments of Mihaly in support of this view, but overlooks the experiments of McIntosh and of Waddell.

W. D. B.

On the influence of non-electrolytes and electrolytes upon the degree of dissociation. *M. Wildermann. Zeit. phys. Chem.* 46, 43 (1903). — It is found that the addition of glycerol does not change the dissociation of dichloroacetic acid or of *o*-nitrobenzoic acid as determined by the freezing-point method, while nitric acid decreases the dissociation of these two acids by the theoretical amount. This is interesting, but one must regret the selection of glycerol. With acetone the results might have been different.

W. D. B.

The electrolytic dissociation of picric acid. *V. Rothmund and K. Drucker. Zeit. phys. Chem.* 46, 827 (1903). — From the distribution of picric acid between benzene and water, the authors calculate a change of dissociation of picric acid with the concentration in the water phase which agrees well with the requirements of the mass law. The dissociations thus obtained do not agree well with those calculated from the conductivity.

W. D. B.

On the pressure and composition of the vapors of solutions in aqueous alcohol. *I. Kablukow, A. Solomonow and A. Galine. Zeit. phys. Chem.* 46, 399 (1903). — The authors find that the relative and absolute partial pressures of water and alcohol vary with nature of the third component added to aqueous alcohol. They explain this by assuming the formation of suitable complexes. The authors are not familiar with the literature of the subject.

W. D. B.

The preparation of mixed ketones by heating the mixed calcium salts of organic acids. *E. B. Ludlam. Jour. Chem. Soc.* 81, 1185 (1902). — When mixtures of calcium salts of organic acids are heated in a bath of boiling sulphur, all three possible ketones are formed, but there is a marked tendency to the formation of the mixed ketone.

W. D. B.

Separation and estimation of silver cyanide and silver chloride. *R. H. A. Plimmer. Jour. Chem. Soc.* 85, 12 (1904). — When a mixture of silver cyanide and chloride is boiled a long time with nitric acid, all the silver cyanide is converted into silver nitrate, while the silver chloride remains unchanged. The principle involved is the same as that made use of by Richards in his separation of hydrochloric and hydrocyanic acids.

W. D. B.

Chemical reactions at very high temperatures. *C. Zenghelis. Zeit. phys. Chem.* 46, 287 (1903). — Aluminum in a heated crucible was burned in oxygen under pressure. The heat thus generated is enough to vaporize platinum and to melt magnesia or lime. When nitrogen is present aluminum nitride is formed. When oxygen close to the burning aluminum is sucked rapidly through a wash-bottle containing a starch iodide solution, an intense blue color is obtained. This is believed to be due to ozone formed at the high temperature. It is unfortunate that the details of this experiment are not given.

W. D. B.

The physical chemistry of the agglutinines. *S. Arrhenius. Zeit. phys. Chem.* 46, 415 (1903). — The author treats a serum as an agglutinin because it has the power of agglutinating bacteria. The measurements of Eisenberg and

Volk on the agglutination of typhoid bacilli by horse serum have been calculated and are found to agree well with the formula

$$C = \text{const. } B^{\frac{1}{2}}$$

in which B is the amount of serum which has reacted with the bacteria and C is the amount of free serum remaining. W. D. B.

**The determination of available plant food in soils by the use of weak acid solvents.** *A. D. Hall and F. J. Plymen. Jour. Chem. Soc. 81, 117 (1902).*— "The authors have compared the amounts of phosphoric acid that could be extracted from nineteen different soils by a 1 percent solution of citric acid, by equivalent solutions of hydrochloric acid and acetic acid, by a saturated solution of carbonic acid, and by an ammoniacal solution of ammonium citrate respectively. Seven of these soils were from plots on the Broadbalk Field, Rothamsted, which had been continuously manured in the same manner for forty-two years previously; the remaining twelve were soils of very varied origin, which had been the subject of crop experiments and whose reaction to phosphatic manuring was well marked.

"In the same seven soils from the Broadbalk Field, the authors determined the potash extracted by the same dilute solvents, with the exception of ammonium citrate; five other soils of different origin, whose response or otherwise to potash manuring had been tested by experiment, were also examined in the same way.

"Determinations were also made of the phosphoric acid and potash dissolved after long digestion with strong hydrochloric acid, of the loss on ignition, and of the earthy carbonates present in each soil.

The authors conclude:—(1). That no sharp line of distinction can be drawn between "available" and non-available phosphoric acid and potash in the soil, and that any process of determining the "available" constituents is an empirical one, dependent on the strength and nature of the acid used.

"(2). That the weak solvents give information as to the requirements of a given soil for mineral manures of a far more trustworthy nature than that which is afforded by such a solvent as strong hydrochloric acid.

"(3). That of the acids examined, the 1 percent solution of citric acid gives results most in agreement with the recorded history of the soil, although there is evidence that the same interpretation cannot be put on results obtained from all types of soil." W. D. B.

#### Velocities

**The rate of decomposition of diazo-compounds.** *J. C. Cain and F. Nicoll. Jour. Chem. Soc. 81, 1412 (1902).*—In most cases the decomposition of the diazo-compounds is described by the equation for a mono-molecular reaction. In certain cases it is shown that hydrolysis causes variations and in certain other cases it is believed that intermediate compounds play a part. W. D. B.

**The decomposition of oxalacetic acid and phenylhydrazone in aqueous and acid solutions and a new method of determining the concentration of hydrogen ions.** *H. O. Jones and O. W. Richardson. Jour. Chem. Soc. 81, 1140 (1903).*— "The rate of formation of pyruvic acid phenylhydrazone is a unimolecular de-

composition of oxalacetic acid phenylhydrazone, quite independent of the ionization of the latter as an acid. The rate of formation of pyruvic acid phenylhydrazone is therefore proportional to the concentration of the oxalacetic acid phenylhydrazone present in the solution at a given time. On the other hand, the production of pyrazolonecarboxylic acid is due to a bimolecular reaction, the rate of formation being jointly proportional to the concentration of the hydrogen ions and to that of the oxalacetic acid phenylhydrazone present in the solution." These two reactions take place simultaneously and are irreversible.

W. D. B.

**Heterogeneous catalytic reactions, I. M. Bodenstein. *Zeit. phys. Chem.* 46, 725 (1903). —**

1. Massive platinum, when sufficiently pure, increases the rate of the formation of water even at ordinary temperatures to a measurable value.

2. When the platinum is at the same temperature as the surrounding medium, a film of liquid water forms on the platinum. Under these conditions the reaction velocity is approximately that of a mono-molecular reaction. The approximate accuracy of this formula, as well as all the observed variations, can be readily explained on the assumption that the reaction actually measured is the rate of solution of oxygen, or occasionally of hydrogen, in this film of water, and that the combustion of the dissolved gases takes place at or in the platinum with a so-called infinite velocity.

3. If the platinum is warmer than the surrounding medium, it will remain dry. The reaction velocity is then increased enormously and the best explanation of the complicated phenomena involves the assumptions: that the rate of solution of the oxygen is the reaction measured; that the rate of combustion of the gases in the platinum is very high, and that the resulting mono-molecular equation is much modified by the air currents caused by the water vapor diffusing away from the platinum.

4. The rate of reaction cannot be decreased much by lowering the temperature or by decreasing the concentration. The platinum was therefore "poisoned" with iodine. With increasing "poisoning" there is decreasing reaction velocity and the results approximate more and more to those required by an equation of the first order.

W. D. B.

**Classification and theory of coupled oxidation and reduction processes. R. Luther and N. Schilow. *Zeit. phys. Chem.* 46, 777 (1903). —** The authors consider the case of three reacting substances giving rise to two reactions. Following the nomenclature of Kessler, they call the substance which takes part in both reactions the "actor", the substance which takes part only in the primary reaction the "inducer", and the substance which takes part only in the secondary reaction the "acceptor". "The reaction between the actor and the acceptor is accelerated when the actor reacts simultaneously with the inducer". If the actor is the reducing agent, the other two must act like oxidizing agents; if the actor is an oxidizing agent, the other two must act like reducing agents. The classification adopted by the authors depends on the nature and the number of the three reacting substances which can exist in three oxidation stages. After a discussion of the various cases arising under this classification, the authors close their article with the following words:

"There is no doubt but that an exact knowledge of the "mechanism" of chemical reactions is the next problem of chemical kinetics, for it is only when a large number of facts have been collected bearing on this point, that it will be possible to attempt the solution of the two fundamental problems of chemical kinetics: the relation of the reaction velocity to the specific nature of the substances, i. e., to the passive resistances; and the relation of the reaction velocity to the potential difference, i. e., to the driving force." *W. D. B.*

**Catalytic oxidation of organic substances by concentrated sulphuric acid.** *G. Bredig and J. W. Brown. Zeit. phys. Chem.* 46, 502 (1903). — The oxidation of aniline and of naphthalene by hot concentrated sulphuric acid is a monomolecular one with many disturbing factors. Copper and mercury sulphates act as catalytic agents, the effect being directly proportional to the concentration. Addition of small amounts of water has no effect. Potassium sulphate and phosphorus pentoxide have no catalytic action but increase the rate by raising the boiling-point. The temperature coefficient is normal between 200° and 300°. Relatively to mercury, copper is a much less efficient catalytic agent with naphthalene than with aniline. A mixture of the sulphates of copper and mercury has a greater catalytic action than would be calculated from the behavior of the single substances. *W. D. B.*

**The influence of persulphates on the catalytic decomposition of hydrogen peroxide by means of colloidal platinum.** *T. S. Price and A. D. Denning. Zeit. phys. Chem.* 46, 89 (1903). — "The velocity of decomposition of hydrogen peroxide is increased by the addition of potassium persulphate. The increase in velocity is probably proportional to the amount of persulphate present.

"The decomposition of the potassium persulphate is very small, its action being for the most part catalytic. Free sulphuric acid also has an accelerating effect on the decomposition and at the same time is itself decomposed.

"It is probable that we have the superposition of two reactions, viz: the catalytic decomposition of the hydrogen peroxide; the reaction between hydrogen peroxide and the persulphates." *W. D. B.*

**The decomposition of chlorates, V.** *W. H. Sodeau. Jour. Chem. Soc.* 81, 1066 (1902). — "The facilitating action of the oxides of manganese is due to the formation of a higher oxide of manganese by the oxidizing action of the heated chlorate and the subsequent breaking up of the higher oxide.

"The liberation of chlorine is not an essential part of the cycle of changes bringing about the facilitation.

"When potassium chlorate is heated by itself, perchlorate is formed by self-oxidation, a process not essentially connected with the evolution of oxygen.

"Addition of manganese peroxide prevents the production of perchlorate by bringing about the decomposition into chlorine and oxygen at a temperature much below that at which self-oxidation of the chlorate proceeds at an appreciable rate." *W. D. B.*

#### *Electrolysis and Electrolytic Dissociation*

**Electrolysis with alternating currents.** *M. Le Blanc and K. Schick. Zeit. phys. Chem.* 46, 213 (1903). — Reviewed (8, 72) from the condensed paper. *Zeit. Elektrochemie*, 9, 636 (1903).

**The electrical conductivity of aqueous solutions at high temperatures.** *A. A. Noyes and W. D. Coolidge. Zeit. phys. Chem.* 46, 323 (1903); *Jour. Am. Chem. Soc.* 26, 134 (1904).—The conductivity of dilute solutions of sodium and potassium chloride has been determined up to 306°, using a platinum-lined steel bomb with quartz insulation. Full details are given in regard to the construction and use of the bomb. In  $n/10$  solutions the percentage dissociation of the two salts is approximately 84 at 18°, 79 at 140°, 74 at 218°, 67 at 281°, and 60 at 306°. Even at 306° the vapor has practically no conducting power. The dilution law holds no better at high temperatures than at low. While an exponential formula will represent the facts at any one temperature, the exponent is not independent of the temperature. The Kohlrausch formula gives by far the best results. *W. D. B.*

**On the electrical conductivity of solutions in sulphocyanates and mustard oils.** *L. Kahlenberg. Zeit. phys. Chem.* 46, 64 (1903).—Experiments were made on the conductivity of ferric chloride and trichloroacetic acid in methyl sulphocyanate, ethyl sulphocyanate, amyl sulphocyanate, and ethyl mustard oil; of silver nitrate in methyl and ethyl sulphocyanate; of mercuric chloride in ethyl sulphocyanate; and of trichloroacetic acid in allyl mustard oil. The conductivity of ferric chloride is of the same order of magnitude as in methyl and ethyl alcohols. The conductivity of the trichloroacetic acid in these solvents is less than that of the best water in contact with air and yet the acid attacks metallic magnesium and dry sodium carbonate. The behavior of ferric chloride is in accordance with the Nernst-Thomson rule; that of trichloroacetic acid is not. *W. D. B.*

**The dissociation constants of oxalacetic acid and its phenylhydrazone.** *H. O. Jones and O. W. Richardson. Jour. Chem. Soc.* 81, 1138 (1902).—At 25° the dissociation constant of oxalacetic acid phenylhydrazone is  $K = 100k = 0.11$ ; for oxalacetic acid the corresponding value is 1.33. *W. D. B.*

**Some observations on the solvent action and electrical conductivity of liquid nickel carbonyl.** *A. Mittasch. Zeit. phys. Chem.* 46, 37 (1903).—All the inorganic salts tested were practically insoluble in liquid nickel carbonyl and had no appreciable effect on its conductivity of  $1 \times 10^{-8}$  reciprocal ohms per centimeter cube. Camphor and alcohol are readily soluble. *W. D. B.*

#### Dielectricity and Optics

**Influence of the electrical discharge from points on the formation and decomposition of gases.** *A. de Hemplinne. Zeit. phys. Chem.* 46, 13 (1903).—One electrode was a point and the other a plate perpendicular to the first. When oxygen is one of the reacting gases, combination takes place more rapidly when the negative electricity streams from the point than when it comes from the plate. This effect is more marked the lower the pressure. A similar, though much slighter, difference is noticed during the synthesis of ammonia. No difference could be detected in the rate of decomposition of ammonia or of carbon bisulphide. In all cases the rate of change is greater, the more luminous the gas becomes. *W. D. B.*

**The decomposition of water vapor by the electric spark.** *D. L. Chapman*

and F. A. Lidbury. *Jour. Chem. Soc.* 81, 1301 (1902). — This is substantially the same as a paper published in *Trans. Am. Electrochem. Soc.* 4, 127 (1903) and reviewed (8, 77).

The influence of solvents on the rotation of optically active compounds, III, IV. T. S. Patterson. *Jour. Chem. Soc.* 81, 1097, 1134 (1902). — A study of the effect of benzene, toluene, mesitylene, the xylenes, and naphthalene on the rotation of ethyl tartrate. With most of these solvents, the ethyl tartrate shows both a maximum and a minimum rotation. As in the previous work, there seems to be a relation between the rotation and the molecular solution volume.

W. D. B.

The absorption spectra of phloroglucinol and some of its derivatives. W. N. Hartley, J. J. Dobbie and A. Lauder. *Jour. Chem. Soc.* 81, 929 (1902). — The spectrum of phloroglucinol in water or alcohol is practically identical with the spectrum of phloroglucinol trimethyl ether. Phloroglucinol in solution must therefore be the enolic and not the ketonic form.

W. D. B.

The determination of avidity by the polarimetric method. J. Walker. *Zeit. phys. Chem.* 46, 30 (1903). — Polarimetric measurements were made on the distribution of sodium hydroxide between acetic and *l*-mandelic acids, malonic and mandelic acids, chloracetic and tartaric acids, and malonic and tartaric acids. The author intends to work further along this line.

W. D. B.

The color changes exhibited by the chlorides of cobalt and some other metals, from the stand-point of the theory of electroaffinity. F. G. Donnan and H. Bassett, Jr. *Jour. Chem. Soc.* 81, 939 (1902). — Transference experiments appear to show that cobalt forms part of a complex ion in the blue solutions. The authors therefore conclude that the blue color of cobalt solutions is due very largely to a blue anion  $\text{CoCl}_2^-$  or  $\text{CoCl}_4^{2-}$  and to the blue undissociated salt  $\text{CoCl}_2$ . This leads to speculations on the constitution of solid  $\text{CoCl}_2$  and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . The color changes with cupric and ferric chloride solutions are believed to be connected with the formation or decomposition of complex anions.

W. D. B.

On color changes observed in some cobalt salts. W. N. Hartley. *Jour. Chem. Soc.* 83, 401 (1903). — The author criticizes some points in the statements of Donnan and Bassett (preceding review). The spectra of aqueous cobalt chloride solutions at different temperatures are not identical with the spectrum of anhydrous cobalt chloride dissolved in alcohol nor with the spectrum of cobalt chloride in hydrochloric acid. The color of the aqueous solutions is believed to be due largely to the presence of a dihydrate, the color of the alcoholic solution to a blue alcoholate which can be isolated and the color of the hydrochloric acid solution to a blue hydrochloride. Black cobalt iodide dissolves in alcohol with an indigo blue color, while the brown hexahydrate gives a green solution identical with the green color of the solid  $\text{CoI}_2 \cdot 2\text{H}_2\text{O}$ , and with the color of the hexahydrate in water when heated above  $50^\circ$  and up to  $100^\circ$ .

Anhydrous cobalt sulphate is rose-pink and can be heated to  $300^\circ$  with

scarcely any perceptible change. When heated to 500° and beyond, it assumes a lilac color, which is due to incipient decomposition. *W. D. B.*

*Crystallography, Capillarity and Viscosity*

**The theory of capillarity and colloidal solutions.** *F. G. Donnan. Zeit. phys. Chem.* 46, 197 (1903). — Starting from the simple Laplace-Gauss theory of capillary forces, the author considers the assumption of negative interfacial tension and the result to which it leads under specified conditions. The theory leads one in certain cases, to predict the spontaneous production of extremely fine-grained heterogeneous mixtures which is exactly what we find in colloidal solutions. This seems to be a very rational method of attacking the problem of colloids. *W. D. B.*

**On the internal friction of solutions.** *J. Wagner. Zeit. phys. Chem.* 46, 867 (1903). — Inorganic salts in aqueous solution do not give values for internal friction which stand in any recognizable relation to the periodic law. A number of cases have been found where mixtures of two non-electrolytes give solutions having a lower internal friction than either of the components. Two instances were also found where the viscosity-concentration curve shows a point of inflection lying between the two end values. Freshly distilled nitrobenzene shows an internal friction which varies with the time. The author is not yet prepared to say that this is due to the existence in equilibrium of two liquid modifications. *W. D. B.*

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## THE ALUMINUM-TIN ALLOYS

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BY E. S. SHEPHERD

A considerable amount of work has been devoted to alloys of aluminum with tin, and certain characteristics have been determined. But there has been some controversy as to whether these metals do or do not form distinct chemical compounds.

Gautier,<sup>1</sup> who first determined the freezing-point curve for these alloys, thought he obtained a maximum at the composition  $\text{AlSn}$ . He classes this series of alloys, as well as lead-copper, and bismuth-copper, among those which give definite compounds. There are, however, some objections to all of Gautier's work. He determined all of his freezing-points with a direct reading pyrometer, reading the galvanometer deflections at regular intervals and from the halt in the rate of cooling the freezing-point could be determined. This method of determining freezing-points is not sensitive, and unless the heat effect is relatively large, no break in the rate of cooling will be found. Furthermore, no provision was made for regular stirring the alloy, and without this no reliable figures can be obtained. This inaccurate reading of temperatures and faulty stirring have vitiated all of Gautier's measurements and led him into serious errors. For example, we need only compare his curves for lead-copper and bismuth-copper with the accurate work of Heycock and Neville, to see just how great his possible errors may be. In both of these cases maxima were obtained, which maxima, as Heycock and Neville have shown, are not maxima, but constant temperatures, due to the existence of two liquid layers. Then, too, he took the freezing-point of copper to be  $1050^{\circ}$ , and determined none of the secondary halts in the cooling curves (i. e., inversion points and eutectics). So that while the measurements were very good at the time they were made,

---

<sup>1</sup> Gautier. *Bull. Soc. d'Encour.* (5) 1, 1293 (1896).

they will all have to be repeated, with modern methods, before we can draw definite conclusions from them.

Campbell and Mathews<sup>1</sup> have also measured the freezing points of these alloys, and while they agree with Gautier as to the maximum at AlSn, they disagree some fifty degrees as to the actual temperatures. Their measurements were made with a recording pyrometer, and in duplicate; they should therefore be reliable. Unfortunately, though, they find a minimum (eutectic) at 500° and at 20 percent aluminum, this eutectic does not appear with any other composition, although they were able to find the 228° eutectic as far over as 75 percent aluminum. If this minimum is real, then all alloys containing more than 20 percent Al must solidify completely at 500° to a mixture of Al (solid solution) and AlSn.<sup>2</sup> There can be no 228° eutectic for these alloys if this minimum is real. Their measurements, however, have shown that in every case between twenty and seventy-five percent of aluminum this 228° eutectic is present and is the *only* eutectic present. Even in the twenty percent aluminum alloys, which is according to them eutectic for AlSn and Al(Sn  $x$  percent) they find the 228° eutectic. Therefore we can say positively from their own measurements that no such minimum exists. As they do not give their method of working, we are at a loss to account for the error in their measurements. It may be due to surfusion, and we will return to a discussion of this later.

From microscopic examination, they are led to believe that tin forms a solid solution with aluminum, with the limiting value at about ten percent tin. There seems to be little doubt as to the accuracy of this observation, though the writer favors

<sup>1</sup> Campbell and Mathews. Jour. Am. Chem. Soc. 24, 253 (1902).

<sup>2</sup> It seems desirable to have some brief method of distinguishing a solid solution from a pure component. The writer would suggest borrowing such a symbol from the mineralogists. Thus for the case of a continuous series of solid solutions as with silver and gold the symbol would be (Ag, Au), while for a case where the solubility of one metal in the other is limited as with aluminum and tin, the expression Al, (Sn, 15 %) would show that the phase was a solid solution of tin in aluminum with a limiting concentration of 15 percent of tin.

a somewhat larger limiting concentration for the solid solution. But one is a little surprised to learn that the  $228^{\circ}$  eutectic is a *single solid solution* and not made up of two constituents.

Guillet<sup>1</sup> has also studied these alloys. By reducing stannic oxide with metallic aluminum he obtains various crystals which could be separated from the alumina and analyzed. He treated the alloys with dilute HCl and then analyzed the crystalline residue. The following table is taken from his paper.

No.	Percent Sn in ingot	Percent Sn in the residue		
		<i>a</i>	<i>b</i>	
1	69.0	75.2	75.9	Superb lamellar crystal Al <sub>3</sub> Sn
2	75.6	86.8	87.1	Filiform and lamellar Al <sub>3</sub> Sn " Al <sub>3</sub> Sn
3	64.5	73.9	73.8	
4	60.9	69.2	69.0	
5	68.2	80.9	81.0	
6	66.6	72.0	71.9	Lamellar and filiform Al <sub>3</sub> Sn
7	38.0	51.8	51.9	

This method of dissolving out the eutectic with acid and analyzing the crystals has already been shown by Le Chatelier to be unreliable. If its results agree with other data it is an interesting coincidence and nothing more. But why throw out analyses 2, 3, and 6 just because they do not calculate to a compound? They are in just as good an agreement as the others and should be given just as much weight. And is it not straining this method to make 1 and 4 Al<sub>3</sub>Sn?

M. Guillet was unable to find any justification for Al<sub>3</sub>Sn either in the freezing-point curve or metallographically. He therefore assumes that Al<sub>3</sub>Sn is formed only at the very high temperature attained in the aluminum reduction. While this is not impossible, it would certainly be worth M. Guillet's while to work out the equilibrium relations between this Al<sub>3</sub>Sn and the freezing-point curve. On the whole, M. Guillet's many compounds of aluminum and the rarer metals would seem to require further verification.

<sup>1</sup> Guillet. Comptes rendus, 133, 935 (1901).



In a recent paper, Anderson and Lean<sup>1</sup> have made some further observations on these alloys. With their observation that aluminum attacks plumbago crucibles readily, the writer is in perfect accord. Not only are plumbago crucibles attacked, but asbestos, and the porcelain tubes of the pyrometer. Consequently it is better to work in crucibles lined with magnesium oxide. To protect the pyrometer tubes, where aluminum is used as a fixed point for calibrating the pyrometer, and also with aluminum rich alloys, it has been found desirable to sprinkle powdered MgO over the surface of the alloy before inserting the pyrometer tube.

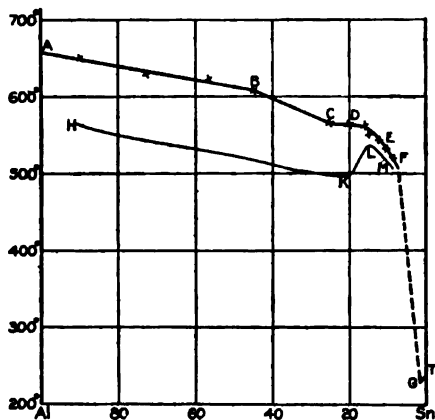


Fig. 1

The freezing-point curve, as determined by Anderson and Lean, is rather interesting. Above forty percent of aluminum they agree very well with Campbell and Mathews, and for that matter with Gautier, but below forty percent they find a different condition of affairs. Between 17.4 and 24.8 percent Al they find a constant temperature at 561°. If this is true, then between 17 and 25 percent Al one would expect to find the alloy separating into two liquid layers. It was to test this point that the writer took up the study of this series. The work was later extended to include the analysis of the solid phase, and the densities.

<sup>1</sup> Anderson and Lean. Proc. Roy. Soc. 72, 277 (1903).

Anderson and Lean determined the freezing-points of various alloys, and plotted these (Fig. 1) as the freezing-point curve or liquidus (A, C, F). They also plotted the temperature at which the rate of cooling again "became normal" and seem to think this indicates the trend of the "solidus" (H, K, L, M). There would seem to have been some misunderstanding as to this, for the curve so obtained certainly does not represent the composition of the solid phase. Its form is due to the fact that all but a few percent of aluminum have crystallized from these alloys above 500° and that these few remaining percents have no appreciable effect on the rate of cooling. Consequently the cooling curve for all alloys above ten percent of aluminum will become "normal" above 500° and the nearer one comes to the tin axis the shorter will be the halt in the cooling curve and the nearer will their line (HKLM) come to the freezing-point curve. The same kind of a line is obtained in the case of lead and mercury, and in this case it is pure metal which separates. In such a case one would hardly speak of the line as indicating the trend of the solidus.

Since their measurements of the freezing-points were determined with a direct reading pyrometer, using small amounts of the alloy and not stirring, it seemed desirable to repeat some of their measurements as a basis for further work. Consequently a series of freezing-point measurements were made.

The alloys were melted up in artificial graphite (nearly free from silicon) or magnesia-lined crucibles. They were kept in an atmosphere of coal gas to prevent oxidation and were stirred by an automatic stirrer during the freezing. Minute nuclei were also added to prevent surfusion. The temperatures were measured by a recording pyrometer of the potentiometer type, which allowed the full scale, 25 cm, to be used for the range of 450–650 degrees. At least three determinations were made of each composition and the calibration repeated for each record. The values obtained are given in Table I.

It is not easy, even when working with such conditions, to get perfectly concordant results, since surfusion occurs with the

greatest ease. With unstirred alloys variations of ten to thirty degrees were sometimes obtained, while with stirred alloys the measurements are fairly constant. To make certain that no change had occurred in the alloy or recorder, one record of the preceding alloy was always run on the plate and then the records of the next higher or lower composition determined. In this way we found that, from ten to fifty percent of aluminum, the increase in aluminum was *always* accompanied by a rise in freezing-point.

TABLE I.

Al	10 per cent	17 per cent	19 per cent	20.8 per cent	25 per cent	30 per cent	35 per cent	40 per cent	50 per cent
Freezing-points	518	545	549	559	566	573	578	582	593
	515	544	551	562	566	573	578	582	593
	516	548	554	559	563	573	579	584	—
	515	544	556	562	566	572	—	584	—
	—	544	554	559	567	—	—	584	—
	—	548	556	—	567	—	—	—	—
	—	548	—	—	566	—	—	—	—
	—	548	—	—	563	—	—	—	—

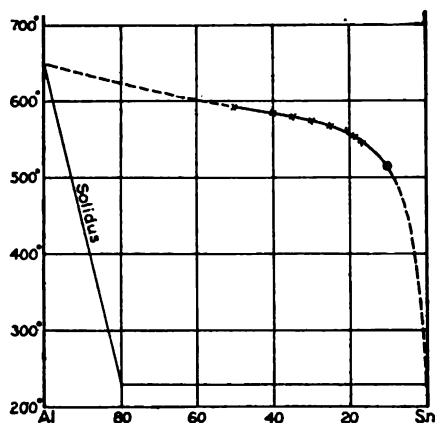


Fig. 2

From the freezing-point curve as we determine it, there is no indication of the existence of two liquid layers. We are entirely unable to verify Campbell and Mathew's minimum at 20 percent Al. This supposed minimum would certainly have

shown up if it really existed. When we consider that on the record the scale was something like one millimeter per degree, and that in over fifty records of the cooling curves no such minimum or second break was found, one may safely conclude that the error lies in the measurements of Campbell and Mathews.

There seems to be no reason to believe that such a compound as  $\text{AlSn}$  has any real existence, at least in so far as the freezing-point curve might indicate it. However, the general flatness of the freezing-point curve might readily suggest that there was an instable region of two liquid layers below the freezing-point curve. Such instances are known for aqueous solutions, and Roozeboom is inclined to believe that a flat freezing-point curve always indicates such an instable field. In cases where the liquids are not transparent the identification of such a phenomenon becomes very difficult. It is the more difficult since the aluminum crystals which separate when freezing begins are lighter and float to the top. Consequently determinations of the composition of the top and bottom of quenched specimens, as well as samples pipetted off from the top and bottom, are liable to error. It seems probable that a better way would be to render these two liquid layers stable by adding a third substance. Such a method has already been used successfully in the case of many aqueous solutions.

The eighteen percent alloy was melted and the alloy held for an hour at selected temperatures and samples pipetted from the top and bottom of the liquid alloy. The temperature was then changed to the next temperature at which a sample is desired, and after standing an hour, the next samples are pipetted off. In this way it seemed probable that if two liquid layers were present they could be easily detected. The values without and with lead are tabulated on the next page.

The samples were taken at higher temperatures because the addition of lead raises the freezing-point.

Another way of testing for the maximum at 18.6 percent Al would be to apply the analytical method of Bancroft. If to

an alloy of aluminum and tin of the composition AlSn, we add say 1 percent of silver and then analyze the mother-liquor after some crystals have separated, the composition of the mother-liquor would lie somewhere on a line drawn through the point

## Percent Al

Temp.	Top	Bottom	Remarks
550°	19.1	18.0	To be expected
560°	18.5	18.4	
580°	18.4	18.5	
590°	18.5	18.0	
640°	18.5	18.5	

## With lead present

570°	19.3	19.6 + 1 pct Pb	
610°	18.6	17.2 + 3 pct Pb	

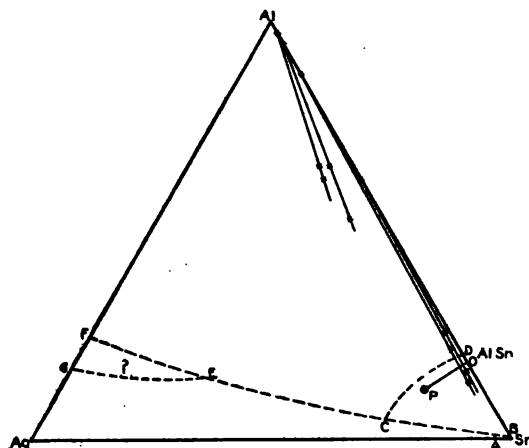


Fig. 3

representing the initial composition and the composition of the solid phase. Such a line is represented by the line (OP) in Fig. 3. This determination was not made, but two others were, which show the same thing. A cooling curve of the alloy was first taken, in order to be sure that during crystallization the

composition of the melt did not meet a boundary curve. It was found that at the lowest temperature at which samples could be pipetted off there had been only one halt in the cooling curve, i. e., the freezing-point.

An alloy of the composition Al 21.83 percent, Ag 1.79 percent, Sn 76.18 percent, was allowed to freeze and the mother-liquor pipetted off after the greatest possible change in concentration had occurred. This mother-liquor was then analyzed. This mother-liquor analyzed Al 13.65 percent, Ag 2.06 percent, Sn 84.29 percent (tin by difference), making the calculation for the composition of the solid phase

$$\begin{array}{rcl} 1. \text{ Al/Ag } 12.1927 & \text{Sn/Ag } 42.5389 \\ 2. \text{ Al/Ag } 6.7719 & \text{Sn/Ag } 41.7919 \\ \Delta \text{Al } 5.4208 & \Delta \text{Sn } 0.7470 & \text{Sn in solid phase} = 12.11 \text{ percent} \end{array}$$

A second determination gave :

Initial concentration : Al 25.80 percent, Ag 0.98 percent, Sn 73.19 (diff.)

Final concentration : Al 16.19 percent, Ag 1.24 percent, Sn 82.30  
Total 99.73.

$$\begin{array}{rcl} 1. \text{ Al/Ag } 26.1766 & \text{Sn/Ag } 74.2490 \\ 2. \text{ Al/Ag } 13.0180 & \text{Sn/Ag } 66.3586 \\ \Delta \text{Al } 3.1586 & \Delta \text{Sn } 7.8906 & \text{Sn in crystals } 37.48 \text{ percent} \end{array}$$

These two analyses when plotted as in Fig. 3 show that there can be no field for the compound AlSn. If such a field existed, it would have caused the change of concentration to follow along a boundary curve as AlSn, Al(Sn 10 percent) (DC), which would have greatly increased the percentage of silver in the mother-liquor. In other words, the change in concentration of the melt passed uninterrupted across the region where AlSn would have been solid phase if there really was a maximum in the freezing-point curve. The provisional boundary curves, based on Gautier's measurements have been drawn in free hand.

These analyses cannot be used to determine the composition of the solid phase since they are so located that a very small error in analysis would cause a great error on extrapolation.

To determine the composition of this solid phase concentrations should be chosen nearer the composition of the phase separating. The following determinations were made:

	Al	Ag	Sn
Initial	65.36	7.07	27.57 (diff.)
Final	62.65	7.77	30.00
1. Al/Ag	9.2383	Sn/Ag	3.8966
2. Al/Ag	8.0655	Sn/Ag	3.8618
$\Delta$ Al	1.1728	$\Delta$ Sn	0.0348
Sn in crystals 2.88 percent			

	Al	Ag	Sn
Initial	65.46	4.92	28.71 = 99.09 pct
Final	52.88	7.16	39.96 (diff.)
1. Al/Ag	13.2956	Sn/Ag	5.8317
2. Al/Ag	7.3863	Sn/Ag	5.5810
$\Delta$ Al	5.9093	$\Delta$ Sn	0.2507
Sn in crystals 4.07 percent			

These values for the percent of tin in the solid phase are not in close agreement, but they serve to show that a solid solution really exists and, considering the unfortunate location of the initial concentrations, they are permissible. Concentrations of about 70–80 percent Al and with 10 and 15 percent Ag should be tried, but the importance of the alloys does not seem to warrant working out this part of the diagram. The other evidence gives the limits of the solid solution very well.

It seemed worth while to determine the densities of these alloys and see what conclusions could be drawn therefrom. Consequently a series of alloys was prepared, chill cast, and the densities determined in dry benzene. The ingots used in determining density averaged about 15 grams in weight.

After the density of the cast alloys had been determined the ingots were annealed two weeks in boiling naphthalene. The densities were again determined, but had not changed sufficiently to warrant giving the measurements. This can be readily accounted for when we recall that the greater part of the

aluminum has crystallized out at a comparatively high temperature and has had rather unusual opportunities to reach equilibrium. Consequently the crystals are practically saturated with tin, even on rapid cooling.

The densities and specific volumes are given in Table II and plotted in Figs. 4 and 5 respectively.

TABLE II.

Percent Al		Sp. V.	Density	Mean density
100	1	0.37130	2.6932	2.680
	2	0.37216	2.6870	
97.7	1	0.36962	2.7055	2.712
	2	0.36874	2.7120	
	3	0.36762	2.7202	
	4	0.36870	2.7120	
95	1	0.36247	2.7588	2.760
	2	0.36232	2.7600	
	3	0.36206	2.7619	
	4	0.36229	2.7602	
90	1	0.35067	2.8517	2.845
	2	0.35179	2.8426	
	3	0.35158	2.8443	
	4	0.35144	2.8450	
80	1	0.33203	3.0117	3.001
	2	0.33285	3.0043	
	3	0.33395	2.9945	
	4	0.33372	2.9965	
70	1	0.31096	3.2158	3.211
	2	0.30998	3.2260	
	3	0.31251	3.1990	
	4	0.31198	3.2053	
60	1	0.28676	3.4872	3.489
	2	0.28647	3.4906	
	3	0.28650	3.4903	
	4	0.28642	3.4914	
50	1	0.26187	3.8187	3.829
	2	0.26417	3.7853	
	3	0.26323	3.7990	
	4	0.25556	3.9130	



TABLE II.—(Continued.)

Percent Al		Sp. V.	Density	Mean density
40	1	0.23855	4.1920	4.199
	2	0.23906	4.1831	
	3	0.23678	4.2233	
	4	0.23821	4.1980	
30	1	0.21418	4.6689	4.671
	2	0.21480	4.6555	
	3	0.21339	4.6874	
	4	0.21391	4.6749	
25	1	0.19938	5.0155	5.012
	2	0.19985	5.0037	
	3	0.19945	5.0139	
	4	0.19933	5.0168	
20	1	0.18776	5.3288	5.306
	2	0.18878	5.2973	
	3	0.18879	5.2969	
	4	0.18850	5.3048	
15	1	0.17679	5.6564	5.670
	2	0.17642	5.6683	
	3	0.17543	5.7004	
	4	0.17680	5.6562	
10	1	0.16228	6.1622	6.176
	2	0.16174	6.1829	
	3	0.16212	6.1684	
	4	0.16157	6.1918	
5	1	0.14995	6.6689	6.679
	2	0.14965	6.6823	
	3	0.14962	6.6835	
	4	0.14958	6.6852	
2.5	1	0.14254	7.0158	7.051
	2	0.14253	7.0161	
	3	0.14223	7.0308	
	4	0.14291	6.9977	

The density curve, while showing that the alloy is less dense than the value calculated, does not possess any minimum

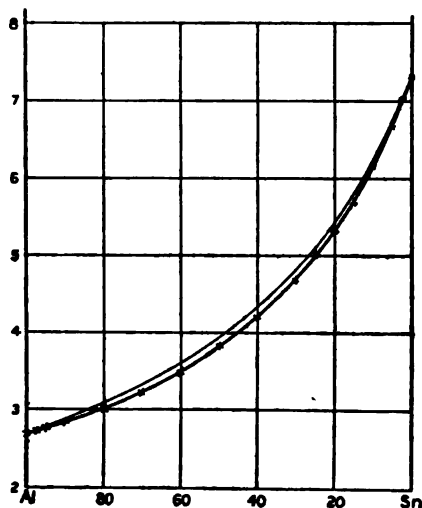


Fig. 4

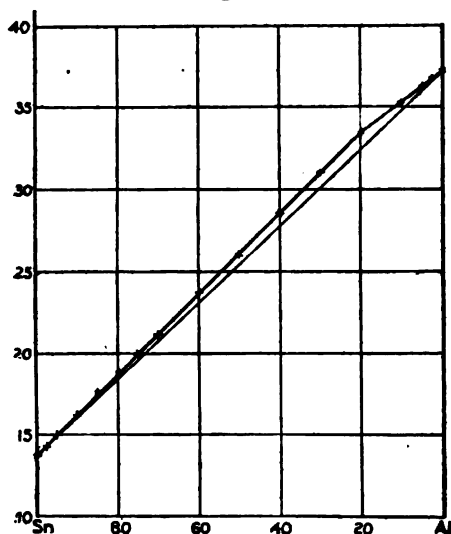


Fig. 5

sharp enough to permit drawing conclusions. The crosses indicate the observed densities. The upper curve is that of the theoretical densities.

When the specific volumes are plotted it is seen that the maximum expansion lies at about 20 percent tin, and it is for this reason that the writer favors this higher value for the limiting concentration of tin in aluminum. This higher concentration is also indicated by the pyrometric measurements.

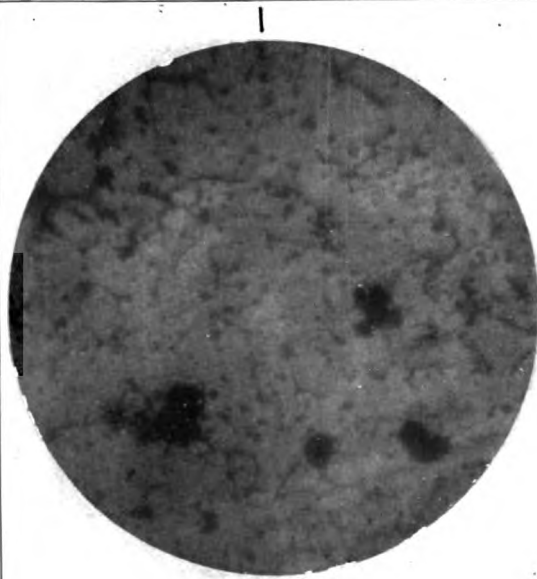
Metallographically the alloy containing 80 percent Al shows no definite eutectic, although very strong etching develops the very indefinite outlines of the crystals of Al, (Sn 20 percent). It is not possible to say that there is or is not a eutectic mass present in this alloy. From the specific volume and pyrometric observations one would not expect the eutectic to appear in alloys of this composition. (Plate I, Fig. 1.)

Polishing in relief produces a fairly definite structure in the case of the 70 percent alloy. (Plate I, Fig. 2.) The photograph shows the harder inter-crystalline mass in relief. This eutectic is not very plentiful, and this fact is a further reason for believing that the limiting concentration for the solid solution is at least 20 percent of tin and below 30 percent. Moreover, since etching should dissolve out the aluminum crystals, the appearance of Fig. 1 would seem to be due rather to the irregular pitting which is common in the etching of solid solutions, the irregularity being due to local galvanic action.

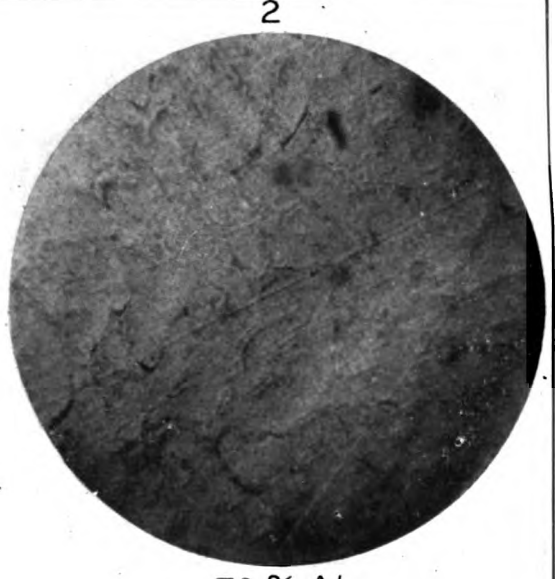
The 20 percent Al alloy is shown in Fig. 3. Large crystalline masses Al(Sn 20 percent) in a ground mass of eutectic. The section was etched with alcoholic HCl, which removed the aluminum-rich constituent, and left the eutectic mass, which is poor in aluminum (0.5 percent), but little attacked. Simple polishing brings out the aluminum as a bright constituent, as shown in Fig. 4.

The polishing of these alloys is difficult owing to the softness of the metal. Since water attacks the alloys, the writer tried polishing powders wet with alcohol and etching in solutions of HCl in alcohol. In this way a bright surface can be obtained.

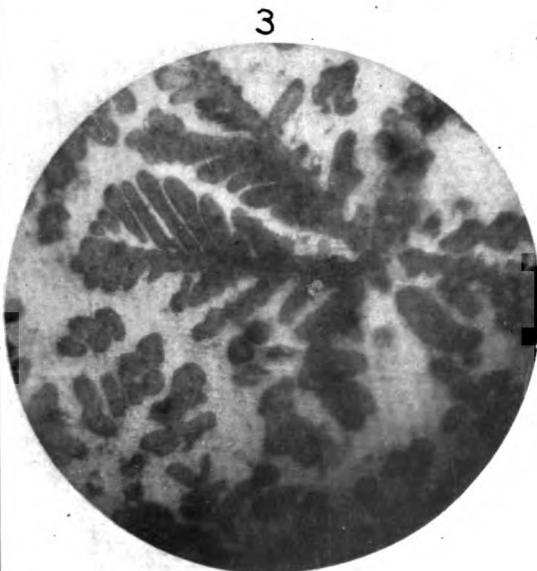
From certain incomplete experiments it seems probable that in the case of the alloys of aluminum and silver the aluminum



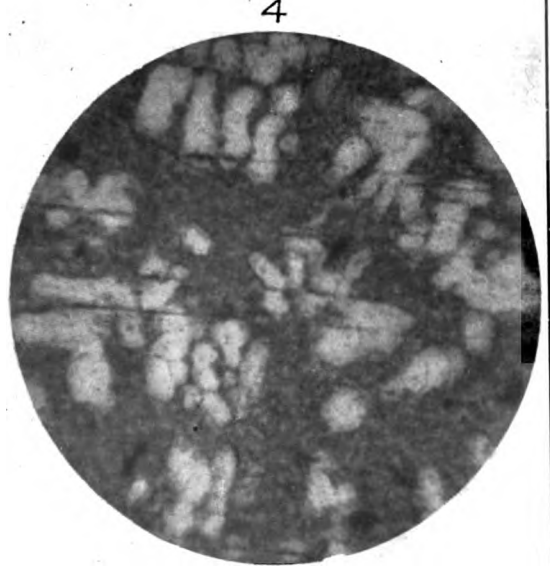
80 % Al  
x450



70 % Al  
x450



20 % Al  
x450



20 % Al  
x450



does not crystallize pure but as solid solution. This would account for the low value obtained for the tin content of the solid phase in the analyses. But as the theory for crystallization in ternary systems has not been worked out for the case of one component forming solid solutions with both the others, it seemed better to wait for this before undertaking further analyses. It would necessitate working out the concentration temperature diagram for at least this field, rather an expensive experiment.

In this investigation it has been shown :

1. That neither  $\text{AlSn}$  nor  $\text{Al}_2\text{Sn}$  exists.
2. That the freezing-point curve has neither a flat due to two liquid layers nor a maximum due to  $\text{AlSn}$ .
3. That the existence of a solid solution has been shown analytically ; and its composition shown to lie at about twenty percent of tin.

The writer wishes to express his indebtedness to Prof. Bancroft for kindly criticism and advice.

*Cornell University.*

## THE TERNARY SYSTEM: BENZENE, ACETIC ACID, AND WATER

BY A. T. LINCOLN

It was shown by Bancroft,<sup>1</sup> about ten years ago, that the condition of equilibrium in a large number of cases of physical reactions could be represented by the Law of Mass Action; that the exponential factors are not necessarily integers and in most cases are not; and that, as in the case of chemical reactions, they are independent of the temperature. He showed that in the case of two non-miscible liquids and a consolute liquid, the equilibria can be represented by the Mass Law Equation, and that there are only two sets of equilibria over the whole range of concentration, and these are represented by two different equations. He has shown the application of the mass law to a large number of other cases of physical reactions, such as, to two partially miscible liquids and a consolute liquid, to the precipitation of a salt by a liquid, to the precipitation of a liquid by a salt, and to the precipitation of one salt by another. In none of these latter cases, however, has the relation between the facts and theory been worked out as yet with a very high degree of accuracy.

In the case of one ternary system, benzene, water, and alcohol, the writer<sup>2</sup> has shown that the Mass Law Equation does represent the conditions of equilibria with a very high degree of accuracy, and that the Law of Mass Action is applicable to this physical reaction, also, that the exponential factors are independent of the temperature as in the case of chemical reactions. Previously, Waddell<sup>3</sup> studied the system, benzene, acetic acid, and water. He concludes from his experiments, that the Law of Mass Action does not apply to this physical reaction, that the equilibria are not represented by simple expo-

<sup>1</sup> Proc. Am. Acad. 30, 324 (1894).

<sup>2</sup> Jour. Phys. Chem. 4, 161 (1900).

<sup>3</sup> Ibid., 3, 233 (1898).

nential formulæ, and that at higher temperatures the deviation from the Mass Law Equation is very much more pronounced than at lower temperatures. In view of the fact that my work had shown such a marked approximation of the experimental results to the values required by the theory in the case of a system analogous to this one with which Waddell worked, it seemed worth while to repeat his work and to ascertain if his conclusions are correct. With this in view the work was undertaken, and the results are given below.

The thiophene-free benzene employed was fractionated and that portion coming over at  $79.5^{\circ}\text{C}$  under a pressure of 755.8 mm was collected and then recrystallized twice. The distilled water of the laboratory was treated with barium hydroxide in contact with which it remained for several days, when it was siphoned off and distilled. This distillate was collected by means of a block tin condenser and only the middle portion of the distillate was collected. A sample of the acetic acid was fractionated a number of times and the portion coming over between  $115^{\circ}$ – $116.5^{\circ}$  was collected and recrystallized many times. This sample had a melting-point of  $14.6^{\circ}$ , and according to Allen,<sup>1</sup> represents a purity of 98.7 percent. On titration with a N/40 barium hydroxide solution it was found to be 98.6 percent pure. In all the following work a correction was made for the water contained in acetic acid of this purity.

All of the flasks and bottles used were thoroughly cleaned and steamed. The bottles in which the benzene, water and acetic acid, as well as the standard solution of barium hydroxide, were stored, were connected with accurately calibrated burettes, which were so arranged that the air which entered the bottles passed through drying vessels containing sulphuric acid or potassium hydroxide. They were, also, so connected that when the burettes were emptied, the air which took the place of the liquid came from the storage bottles. By these precautions the solutions were thoroughly protected during the series of experiments.

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<sup>1</sup> Commercial Organic Analysis, I, p. 387.



The determinations were made in 50 cc flasks (or in 200 cc flasks) which had been thoroughly cleaned and steamed. Into one of the flasks were introduced 5 cc of acetic acid (or 100 cc) and to this was added a definite quantity of benzene, and then enough water was introduced to produce clouding at room temperature. The mixture was then warmed up a few degrees above the temperature at which the determination was to be made. When the contents of the flask became homogeneous the flask was transferred to a bath which was kept at the desired temperature. After remaining in the bath long enough to acquire the temperature of the same, if clouding did not result, the flask was removed, and a few drops of water added from the burette, and the flask warmed until the contents became homogeneous, when it was returned to the bath and allowed to remain with occasional shaking until it had acquired the temperature of the bath. If clouding did not result, this process was continued until it was found that one drop of water caused the second liquid layer to appear. In order to ascertain this point the flask had to be removed from the bath in which it was kept. So in order to make the observation and at the same time prevent the clouding resulting from cooling the walls of the flasks by contact with the air, the flasks were placed in a beaker in the bath and the beaker containing the flask and water from the bath was removed and the observation made.

The bath employed was an ordinary Ostwald thermostat provided with a water turbine for stirring and no difficulty was experienced in keeping the temperature constant to within a few hundredths of a degree.

In the manner just described the data given in the following tables were collected. In Table I are the data for the equilibrium determinations at 25° C and the calculated values for the amount of water that should have been found and also the values of the constant are given in the last column. The headings of the other columns are self-explanatory.

In Table II are given the data for the determinations made at 35° C. The headings of the columns are self-explanatory

except the column marked 3, which contains the values found in order to produce the same degree of clouding. We shall refer to this subsequently.

TABLE I.

Temperature 25°

 $x$  = cc benzene,  $y$  = cc water per 5 cc acetic acidFormula  $n \log x + \log y = \log C$  $\log C = 0.2875$  ;  $n = 0.6136$ 

$x$ benzene		$y$ water		$\log C$
		Found	Calculated	
1	10.06	0.45	0.445	0.2829
	10.06	0.45	0.445	0.2829
2	8.04	0.57	0.54	0.3114
	8.04	0.55	0.54	0.2959
	8.04	0.55	0.54	0.2959
3	6.03	0.64	0.64	0.2850
	6.03	0.62	0.64	0.2710
4	5.03	0.72	0.72	0.2878
	5.03	0.69	0.72	0.2694
	5.03	0.70	0.72	0.2756
5	3.02	0.99	0.98	0.2903
	3.02	0.97	0.98	0.2814
6	2.51	1.12	1.10	0.2947
	2.51	1.12	1.10	0.2947
7	2.01	1.29	1.26	0.2966
	2.01	1.27	1.26	0.2898
8	1.51	1.47	1.50	0.2771
	1.51	1.49	1.50	0.2830
9	1.01	1.93	1.93	0.2882
	1.01	1.87	1.93	0.2745
10	0.80	2.23	2.22	0.2889
	0.80	2.20	2.22	0.2830

TABLE I.—(Continued).

Formula  $n' \log x + \log y = \log C' = 0.244$ ;  $n = 0.9166$ 

	$x$ found	$y$ found	$x$ calc.	$y$ calc.	$\log C'$
11	0.60	2.81	0.608	2.80	0.2438
	0.60	2.80	0.599	2.80	0.2453
12	0.50	3.26	0.510	3.31	0.2373
	0.50	3.25	0.511	3.31	0.2360
13	0.35	4.55	0.320	4.59	0.2401
	0.35	4.53	0.321	4.59	0.2382
14	0.23	6.82	0.228	6.75	0.2487
	0.22	6.82	—	7.00	0.2310
15	0.17	9.53	0.158	8.91	0.2738
	0.16	9.53	—	9.42	0.2496

One of the greatest difficulties to be contended with in the experimental work was obtaining the point of equilibrium. It was difficult to detect the appearance of the second liquid layer as it did not manifest itself in the same manner over the whole range of concentration. Over one portion there was first a very slight opalescence which, upon further addition of water, increased until a decided cloudiness resulted, and finally the second liquid layer was very apparent. Over the other portion of the concentrations where the water was in excess of the benzene, the second liquid layer appeared as fine clear globules which floated on the surface, thus indicating that it was the benzene layer that was separating out. Owing to these two different appearances of the second liquid layer, it was somewhat difficult to determine the true point of equilibrium.

It was no doubt this difficulty which presented itself to Waddell when he determined the equilibrium of the system benzene, acetic acid and water, for he states that he took as the end-point, i. e., as the point of equilibrium, the same degree of clouding. That one cannot use the same degree of clouding as the end-point for the establishment of equilibrium is very apparent

TABLE II.

Temperature 35° C

 $x$  = cc benzene,  $y$  = cc water, per 100 cc acetic acidFormula  $n \log x + \log y = \log C = \text{Mean} = 0.810$ .  $n = 0.610$ 

	(1) $x$ found	(2) $y$ found	(3)	$y$ calc.	$\log C$
1	18.10	1.16	—	1.11	0.8322
	18.10	1.12	—	1.11	0.8169
2	16.09	1.22	1.26	1.23	0.8061
	16.09	1.21	1.26	1.23	0.8025
3	10.06	1.56	1.79	1.58	0.8051
	10.06	1.54	1.81	1.58	0.7995
4	6.03	2.18	2.30	2.16	0.8148
	6.03	2.17	2.30	2.16	0.8128
5	4.02	2.77	—	2.76	0.8113
	4.02	2.78	—	2.76	0.8129
6	3.01	3.27	—	3.30	0.8067
	3.01	3.25	—	3.30	0.8040

Formula  $n' \log x = \log y = \log C' = \text{Mean} = 0.842$ .  $n = 0.92$ 

			$x$ calc.	$y$ calc.	$\log C'$
7	1.00	7.01	1.01	6.95	0.8457
	1.00	7.00	1.01	6.95	0.8451
8	0.65	10.10'	0.666	10.33	0.8322
	0.66	10.10	0.666	10.19	0.8383
9	0.48	13.64	0.480	13.65	0.8416
	0.47	13.64	0.480	13.92	0.8331

from the fact that in one portion of the series of concentrations there is a decided clouding, while at the other end of the series there is no clouding, but the separation of the second liquid layer as clear transparent globules. In that portion of the concentrations where decided clouding does take place, the same de-

gree of clouding does not represent the points of equilibrium. For example, in one experiment, No. 3 at  $30^{\circ}$ , it requires 1.56 cc of water to produce a decided opalescence and 1.79 cc to produce a decided clouding, while in another experiment opalescence was produced by the addition of 2.18 cc, while the same degree of clouding as in the preceding experiment was produced by 2.30 cc of water. The calculated value in the first case was 1.58 cc and in the second 2.16 cc of water. In Table II, column 3, are the values of the quantities of water that were required to produce the same degree of clouding in these various cases. By comparison with the corresponding values in column 2 it will be observed how much more was required than that just necessary to produce the decided opalescence which we took as the indication of the appearance of the second liquid layer, that is, as the point of equilibrium. From this I think we are justified in concluding that Waddell's results are wrong. He was not working with a system in equilibrium, but had an excess of one of the components, and for that reason we could not expect the results to conform to the law of Mass Action.

If we apply the law of Mass Action to the data given in the tables above wherein we let  $x$  = cc of benzene,  $y$  = cc of water, and  $z$  = cc of acetic acid, then our equation takes the form  $x^{\alpha}y^{\beta} = z^{\alpha+\beta}$ . Since the acetic acid was kept constant and we have  $x^{\alpha}y^{\beta} = C^{\gamma}$ , and if we define  $\alpha/\beta = n$ , our equation then takes the form  $x^n y = C$ , or expressed logarithmically, we have  $n \log x + \log y = \log C$ . Now this is in the form of the equation of a straight line wherein we have the logarithm of the quantities in place of the quantities themselves. Hence, if we plot the logarithm of the quantities of benzene and water used, the resulting curve should be a straight line with the slope  $n$ . From this curve the value of  $n$  can be determined, which in the case of the determinations at  $25^{\circ}$  C given in Table I are plotted on Fig. 1. It will be readily seen that we have two distinct curves and that one curve does not represent the condition of equilibrium over the whole range of concentration; but confirms Bancroft's statements that for two non-miscible liquids and a consolute liquid there are two sets of equilibria, and we have

two curves corresponding to these two sets of equilibria. Further, the different end-points seem to correspond with these two sets, for over the greater part of one we get the second liquid layer appearing as fine transparent globules and over a considerable part of the other as an opalescence. Having determined the values for  $n$  and  $n'$ , we then have the distinct curves of different slopes. If now we substitute the value of  $n$  and  $n'$  in their respective equations we obtain the values for  $\log C$  and  $\log C'$  as given in the last column. If the mean value be substituted in our formula and we solve for the value of the amount of water that should have been added, we obtain the values given in column *y calc*, which agrees fairly well with those found experimentally and given in column 2. Under *x calc* are given the calculated values for benzene, assuming the value of  $y$  known.

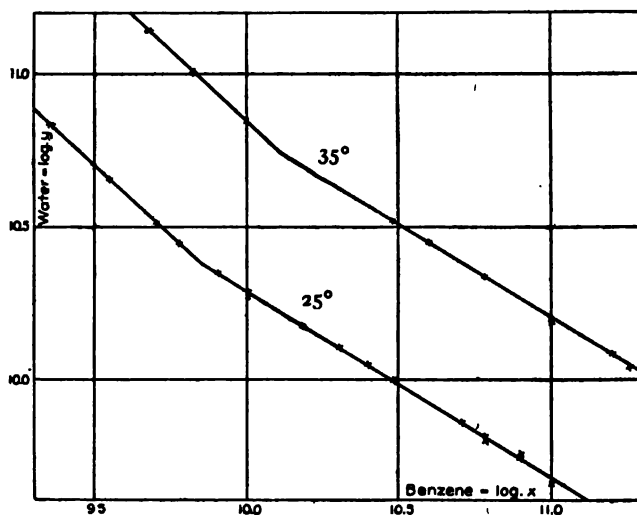


Fig. 1

If this physical reaction follows the Mass Law the exponential factors should be independent of the temperature, i. e., the values of  $n$  should be the same at whatever temperatures the equilibrium is established. Waddell states that at 35° C the deviation of this equilibrium from the Mass Law is even more

pronounced than at 25° C. A series of determinations was made at 35° C and the results are given in Table II, and the plotted results are represented in Fig. 1. It will be observed that there are two curves corresponding to the two equilibria and further the value of  $n$  (0.61) at 35° is very nearly the same as  $n$  (0.6136) at 25°, while the values for  $n'$  (0.92 against 0.9166) are almost exactly the same at both temperatures. Hence it seems that we are justified in concluding that the temperature does not affect the value of the exponential factor and that this physical reaction between benzene, acetic acid and water conforms to the Mass Law Equation.

In this paper we have shown :

1. That Waddell was wrong in selecting the same degree of clouding as the point of equilibrium in the system benzene, acetic acid and water.
2. That equilibrium in the system benzene, acetic acid and water can be represented by the Mass Law Equation.
3. That for the range of temperature from 25° to 35° the exponential factor is constant, as in the case of chemical reactions.

I wish to express my gratitude to Mr. J. V. Mapes, who did a part of the experimental work herein presented.

*University of Illinois,*

*Feb., 1904.*

# CRYSTALLIZATION IN THREE-COMPONENT SYSTEMS

BY WILLIAM C. GEER

## I. INTRODUCTION

The majority of chemists who have studied three-component systems have contented themselves with investigations of the equilibria established between the phases of the systems considered. They have determined the fixed points, boundary curves and isotherms, with the consequence that their results were plotted graphically in diagrams. However, the discussions which followed have consisted quite largely of proofs that the data deduced were in agreement with the conclusions from thermodynamic principles.

From the point of view of pure theory such statements of facts and principles may be the really legitimate object of research of this kind. Nevertheless, to the end that these data may be utilized in practical work, it seems desirable that they be considered from the standpoint of one who would know what is the composition of the phases which separate when ternary systems are cooled. In some instances crystallization experiments have been made and published, and the data rendered available for study. The systematic elaboration of the theory of phase separation has never been carried out.

Therefore, it is the purpose of the present paper to discuss crystallization in ternary systems and to point out certain peculiarities which would scarcely be expected from a cursory review of the current data. The chief reliance will be placed upon certain typical cases, using the triangular diagram. Having drawn such general and special conclusions as may be done by non-mathematical methods, the theory thus deduced will be applied to the study of some actual data taken from the published investigations. By means of this theory the composition of the phases which separate from solutions of assumed concentration, when cooled to successive temperatures, will be predicted.



## II. FUNDAMENTAL PRINCIPLES

The simplest and most convenient method of representing the equilibria between three components, without a consideration of the vapor phase, is by means of the triangular diagram of Roozeboom<sup>1</sup> and Bancroft.\*

Let the pure components be given by the apices of an equilateral triangle, the invariant systems by points (quintuple points), the univariant systems by lines (boundary curves), and the divariant systems by fields included within the triangle, and there is obtained a complete and easily comprehensible picture of the equilibria existing between the phases involved in the system in question. By the aid of this diagram the theory of crystallization is deduced.

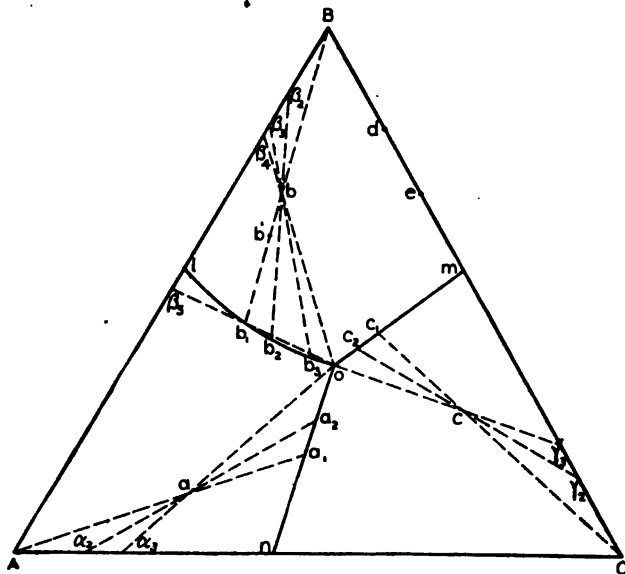


Fig. 1

I. *Systems without Compounds.*—In Fig. 1 is plotted an ideal case of a system consisting of three components, A, B, and C, which unite to form no compound, either binary or ternary, and

<sup>1</sup> Zeit. phys. Chem. 15, 13 (1894).

\* Jour. phys. Chem. 1, 403 (1897).

no solid solution. From the diagram one may infer that  $l$ ,  $m$ , and  $n$  are the points representing the quadruple points of the respective binary systems, and  $o$  is the quintuple point.

From the deductions of van Rijn van Alkemade, Schreinemakers and others, it is known that the temperatures fall along the sides of the triangle toward the binary eutectic points and, so far as this figure is concerned, toward the ternary eutectic.

When a saturated solution is cooled and a solid crystallizes, the concentration of the solution changes by the amount of the separated phase. In other words, the difference between the number of kilograms of A, B and C in the original solution and the number of kilograms of A, B and C in the new solution is the number of kilograms of A, B and C in the solid crystallized. If one starts with a concentrated solution and cools, the new solution which results from the crystallization lies on a straight line which passes through the point giving the composition of the solid and the point giving the composition of the initial solution. Such change of concentration along a straight line through the initial solution and the solid crystallized, constitutes the fundamental principle of phase separation. In the form here applied it is but a restatement of the principle used recently by Bancroft,<sup>1</sup> and others.\*

Thus, in Fig. 1, from a solution which has a composition represented by the point  $d$ , on the side of the triangle BC, the component B will separate, on cooling, while the solution itself will change concentration in the opposite direction along the line BC. At some temperature, lower than that of the original solution, there exists, in equilibrium with B, a new solution  $e$ .

From the diagram one may find the data which will enable him to compute the amount of B which has separated from the solution and also the amount of B retained in the solution  $e$ . The ratio of the line  $de$  to the line  $Be$  is the percentage of the total composition of the solution  $d$ , which has separated as B in cooling from  $d$  to  $e$ . The ratio of  $Bd$  to  $Be$  is the percentage of

<sup>1</sup> Jour. Phys. Chem. 6, 178 (1902).

\* Browne. Ibid. 6, 287 (1902). Shepherd. Ibid. 6, 519 (1902).

the total composition of  $d$ , which remains in the solution  $e$ . Numerically, the composition of  $d$  is 80 percent B and 20 percent C. Assume it to consist of 80 kilograms of B and 20 kilograms of C. At  $e$  the percentage composition is 70 percent B and 30 percent C. The number of kilograms that have separated is found by the ratio

$$\frac{de}{Be} \times 100 = \frac{10}{30} \times 100 = 33\frac{1}{3} \text{ percent.}$$

Thus,  $33\frac{1}{3}$  percent of 100 kilograms, or  $33\frac{1}{3}$  kilograms, have separated as B, and  $66\frac{2}{3}$  percent, or  $66\frac{2}{3}$  kilograms of B and C remain in  $e$ . The solution  $d$  contains 80 kilograms of B.  $80 - 33\frac{1}{3} = 46.6$  kg of B remain in  $e$  with the original 20 kilograms of C. The percentage of B and C in  $e$  may be checked from the figures given. Solution  $e$  contains

$$46.6 \text{ kg B} + 20.0 \text{ kg C} = 66.6 \text{ kg};$$

$$\frac{46.6}{66.6} \times 100 = 70 \text{ percent B};$$

$$\frac{20}{66.6} \times 100 = 30 \text{ percent C.}$$

If the solution  $e$  is cooled further, B continues to separate until  $m$  is reached. Since this is the cryohydric temperature, pure B and pure C separate together with no further change in the concentration of the solution.

Within the field  $Blom$ , solutions containing the three components will be in equilibrium with B. If a solution, which is given a composition, represented by a point  $b$ , is cooled, B will crystallize, while the composition of the new solution will be indicated by a point on a straight line passing through  $b$  and the point giving the composition of the phase separating, viz., B, at the apex of the triangle. If the solution is cooled further, each successive, so-called "new solution" will have its composition given by a point on the straight line through  $b$  and B, until finally a solution  $b_1$  will appear whose composition is found on the boundary curve  $lw$ . The line  $bb_1$  is, therefore, the locus of the points which give the compositions of the successive solu-

tions which are formed from the original solution  $b$ , on cooling, with the separation of B as solid phase.

The amount of B, which has crystallized, is computed in the manner previously indicated. In cooling from  $b$  to  $b'$ ,  $\frac{bb'}{Bb'} \times 100$  percent of the solution having the composition  $b$  has

separated as B. So, also,  $\frac{bB}{Bb'} \times 100$  percent of the original solution  $b$  remains as a solution having the composition  $b'$ . In the case of the solution  $b_1$ ,  $\frac{b_1b}{Bb_1} \times 100$  percent of the solution  $b$  has

separated as B in cooling from  $b$  to  $b_1$ . From the phase rule definition of univariant systems the solution  $b_1$  is in equilibrium with B and A. Therefore, if the temperature be again lowered a mixture of A and B must crystallize.

It has been stated that a straight line joining the points representing the composition of a solid phase and that of the solution, from which it has separated, will pass through the point representing the composition of the new solution resulting. The converse is true, which is the form of the principle applied by Bancroft<sup>1</sup> in his synthetic analysis of solid phases. If a given solution is cooled from one temperature to another, a straight line joining their respective compositions will on extrapolation pass through the point which gives the mean composition of the solid which has separated. In the cases thus far considered this mean composition is none other than that of a pure component. However, when two phases separate together, as the components A and B along the boundary  $bo$ , the mean composition of the solid which separates in cooling between two temperatures, provided no solid is removed during the process, will be found as a point on the line joining the points which give the composition of the constituent phases. In the case mentioned, this line is the side of the triangle AB. This line may connect pure components, a component and a compound, or two compounds.

Since the mean composition of the solid separating is to be

<sup>1</sup> Jour. Phys. Chem. 6, 178 (1902).

found on the line joining the compositions of the constituent phases and also on the extrapolated portions of the line through the composition of the two solutions, it follows that this mean composition desired lies at the intersection of these two lines. Therefore, a line joining  $b$  and  $b_2$ , in Fig. 1, will extrapolate to  $\beta_2$ , on the line AB, which gives the mean composition of the solid which has separated on cooling the solution  $b$  from the temperature of the isotherm passing through that point to the temperature of the isotherm passing through  $b_2$ . The mean composition of the phases which have crystallized in passing from  $b$  to  $b_2$  is, by the same reasoning,  $\beta_2$ . In cooling from  $b$  to  $o$  a solid  $\beta_4$  separates. After the temperature of the quintuple point  $o$  is reached, the component C appears as a phase in the solid which is crystallizing. From the definition of the eutectic point the solution and solid are of the same composition, so that no further concentration change can occur.

At any intermediate temperature the same laws are applicable. A solution of concentration  $b_1$  on cooling to  $b_3$  is seen from the diagram to be similar to those mentioned above. Since the two solutions lie on the boundary curve, A and B crystallize together. Extrapolation through  $b_1$  and  $b_3$  to the side of the triangle AB gives  $\beta_3$ , which point shows the mean composition, in A and B, of the solid which separated during the cooling from  $b_1$  to  $b_3$ .

The amount of solid which has separated between two points is computed in the manner previously described. The fraction of the solution  $b$  which separates as B in cooling from  $b$  to  $b_1$  has already been shown by the ratio

$$\frac{b_1 b}{B b_1}.$$

In like manner the fraction of  $b$  which has separated as A and B mixed, between the temperatures of  $b$  and  $b_2$ , is found by the ratio

$$\frac{b b_2}{\beta_2 b_2}.$$

The fraction of the original solution  $b$  which remains in solution  $b_2$  is indicated by the ratio

$$\frac{\beta_2 b}{\beta_1 b_1}$$

The same method holds for the other temperatures and between any two temperatures. From the fundamental principle of solid separation mentioned on p. 259, it follows that

$$\frac{b b_1}{\beta_1 b_1} + \frac{\beta_1 b}{\beta_1 b_1} = 1.$$

Or, when expressed in percentages, their sum is one hundred percent. The same conclusion is also evident geometrically.

The expression *crystallization curve* will be used to denote the locus of the points which represent the compositions of the solutions formed on cooling any given solution from any given temperature to the quintuple point at which it becomes solid, under the assumption that no phase is removed during the cooling. The crystallization curve in the figure discussed begins with  $b$ , is a straight line to  $b_1$ , turns sharply at that point and follows the boundary curve to  $o$ . From any point on the crystallization curve a line drawn through the initial solution will extrapolate back to the point which represents the mean composition of the solid phase which has separated during the cooling. Thus the line from  $b_1$  to  $b$  extrapolates to  $B$ ; from  $b_2$  to  $b$  extrapolates to  $\beta_2$ ;  $b_3$  to  $\beta_3$ ; etc. When the point  $o$  is first reached, the solid phase has the composition  $\beta_4$ . As the solution solidifies, the composition of the solid phase changes from  $\beta_4$  to  $b$ , reaching  $b$  as the last drop of solution disappears.

From solutions in the other fields, such as  $a$  and  $c$ , similar crystallization curves are obtained and similar conclusions may be deduced. The phases which appear on allowing solution  $a$  to crystallize will be, first pure A, then a mixture of A and C, and finally a mixture of A, B and C.

2. *Systems with Compounds*. —When two of the components in a ternary system unite to form a binary compound, the theory is deduced in accordance with exactly the same methods. The binary compound may be one of two types; it may be stable at its melting-point, or, it may be instable. Ideal diagrams will be discussed for each kind of compound.

## First Case

In Fig. 2 is drawn an illustration of the former case. The point D indicates the composition of the compound. The principles are applied as in the previously discussed simple case. Inasmuch as pure B coexists with solutions within the field  $B|pom$ , that phase will separate when the solution indicated by  $a$  is cooled. The composition of the solution itself will change along the crystallization curve  $aa_1$ , and will meet the boundary curve  $om$  at  $a_1$ . Both B and C crystallize on continued cooling, and the solution changes along the boundary to the eutectic point  $o$ , at which the compound D begins to separate with B and C. The composition of the solid which has separated from  $a$  is found by extrapolating from any point on the crystallization curve through  $a$  to the line joining the composition of the phases which separate. The dotted lines in the figure show such extrapolation.

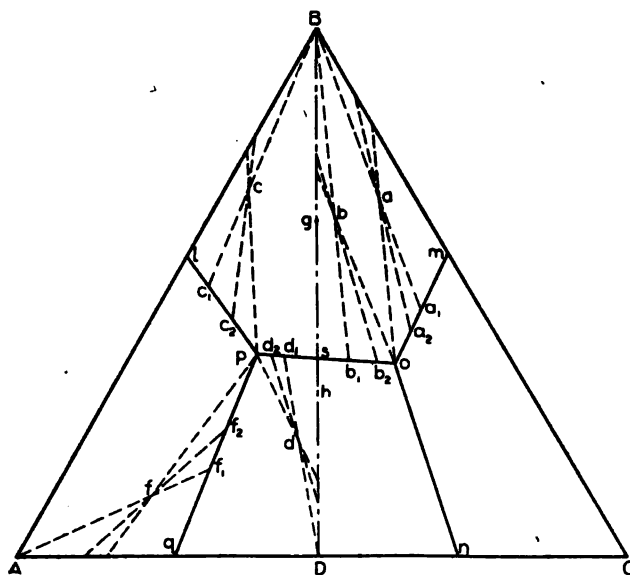
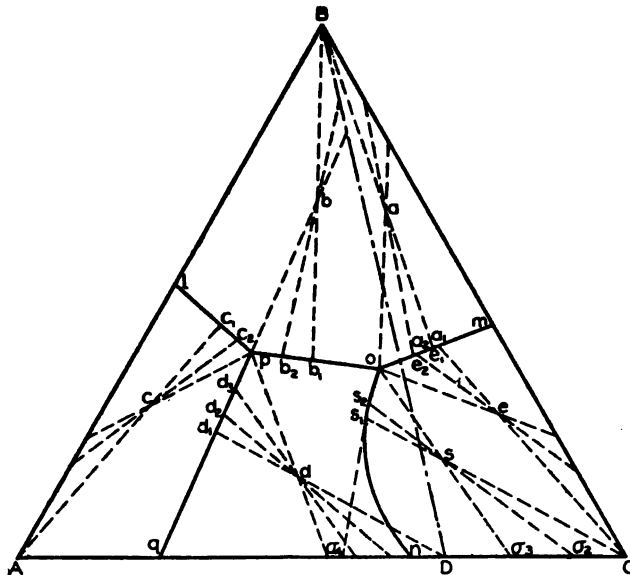


Fig. 2

In like manner, from solution  $c$ , B will appear first, then a mixture of B and A, and finally, at the eutectic  $p$ , a mixture of B, A and the compound D. The course of the crystallization

curve is from  $c$  to  $c_1$ ,  $c_2$ , and finally  $p$ . So also, from solution  $f$ , A separates first, then A and D, and finally A, D, B.

From any solution in the field  $B\text{lpom}$  pure B will separate. From an initial solution  $b$ , B will crystallize pure from  $b$  to  $b_1$ . When the crystallization curve reaches the boundary  $po$ , at  $b_1$ , D separates with B. The lines carried back from  $b_1$ ,  $b_2$  and  $a$ , which are points on the crystallization curve, intercept, in this case, not the side of the triangle, but the line BD. BD is the line which joins the composition of the two phases that separate. From any solution, as  $g$ , on this line, B will separate until the boundary is reached at  $s$ , at which point B and D will crystallize together and the solution will go solid at the temperature of that point, with no further change in concentration. The same is true of the solution  $h$ , in the field  $q\text{pom}$ , from which D will first separate and then B and D. From solution  $d$ , D will separate first, the crystallization curve ending, as shown, at  $p$ .



**Fig. 3**  
**Second Case**

The second case of the systems wherein a binary compound exists, is illustrated by Fig. 3. The compound is instable at its



melting-point. Consequently, the point D lies without the field in which the compound is in equilibrium with solutions.

Pure B will separate from a solution of composition given by  $a$ , in the field  $B\ell pom$ , and the crystallization curve will extend from  $a$  to  $a_1$ ,  $a_2$  and to  $o$ . The composition of the solid is found as before, by carrying back the lines joining the concentration of the initial and final solutions. These extrapolations intercept the side BC at the points shown in the figure.

From  $a$ , the components B and C will separate until the crystallization curve reaches the quintuple point  $o$ . At  $o$ , C begins to unite with A to form the compound D. If the concentration of the original solution was such that A all disappears from the solution before C from the solid, then the solution goes solid at  $o$ , which becomes the end of the crystallization curve. If, however, C disappears first, the crystallization curve follows the boundary curve  $op$  to  $p$ . As a matter of fact, solutions which start in that part of the field to the right of BD will go solid at  $o$ , those which start on the left of BD will go solid at  $p$ . Solution  $a$ , then, becomes solid at  $o$ .

From a solution  $b$  the component B will separate, then the compound D with B along the crystallization curve from  $b_1$  to  $p$ . At the latter point B, D and A will precipitate together. The solution will become solid at  $p$ , which is the end of the crystallization curve that began at  $b$ .

A solution in the field  $A\ell pq$  will act in a similar manner. From the solution  $c$  the component A will separate until the crystallization curve reaches the boundary  $\ell p$  at  $c_1$ . Further cooling causes B to crystallize together with A. The crystallization curve thus follows the boundary curve  $\ell p$  to  $p$ . At  $p$  the compound D appears. Since  $p$  is the minimum quintuple point, the solution goes solid at that temperature, due to the separation of A, B and D. The final composition of the solid is that of the initial solution  $c$ .

In the field  $qpon$  the compound D will be the first phase to crystallize. From such a solution as  $d$  the compound D will separate and the crystallization curve will extend from  $d$  to  $d_1$ ,  $d_2$ , and finally end at  $p$ .

In the field *Cmon* a condition is found which requires a distinction between two cases. From a solution having a composition given by  $e$ , C will crystallize. The crystallization curve then follows the boundary curve, B and C separating, through  $e_1$ ,  $e_2$  and  $o$ . The crystallization curve ends at  $o$  for the reasons mentioned when considering the solution  $a$  in the same figure, viz., A disappears from the solution sooner than C from the solid, so that solidification occurs.

C separates from the solution  $s$  until the crystallization curve reaches the boundary curve *on* at  $s_1$ . From the latter point the boundary curve is followed to  $o$ . As is seen from the lines which join  $s_1$ ,  $s_2$  and  $o$ , respectively, to  $s$  and are extrapolated until they intersect the side of the triangle AC, the solid consists of D and C.

As the solution changes composition along the boundary curve *no* from  $s_1$ ,  $s_2$ , to  $o$ , it is seen from the figure that the solid changes composition from C,  $\sigma_2$  to  $\sigma_3$ . While cooling from  $s_1$  to  $s_2$  the total solid which has separated from  $s$  changes composition from C to  $\sigma_2$ . The solid which separates from  $s_1$  during the cooling to  $s_2$  is found by extrapolation of the line joining  $s_1$  and  $s_2$ , and is  $\sigma_4$ . However,  $\sigma_4$  lies outside the line joining the phases which separate, viz., DC. Thus, by no possible combination of C and the compound of A and C, viz., D, can a mixture be made which has a concentration  $\sigma_4$ . Therefore, D and C cannot have separated together during the cooling from  $s_1$  to  $s_2$ , nor, on extension of the reasoning, during the cooling to  $o$ ; but, on the contrary, C has been disappearing and D separating alone. If C disappears from the solid faster than D is formed, then C must in reality be dissolving as well as uniting with A to form D. From the solution  $s$ , then, C will crystallize until the crystallization curve intercepts the boundary curve *on* at  $s_1$ . From  $s_1$  to  $o$ , C will, wholly or in part, disappear and the compound D will crystallize. On reaching  $o$  the concentration of the solid is  $\sigma_3$ . The temperature will now remain constant while B crystallizes with D. Since the concentration of A in the original solution is low, the A is used up in forming D before the solid C can disappear and, consequently, the composi-

tion of the solid changes from  $\sigma_3$  to  $s$ , reaching the latter point as the last drop of the solution becomes solid at  $o$ .

If  $s_1$  and  $s_2$  are made to approach each other along the curve  $on$ , the line  $s_3, s_1, \sigma_4$  approaches the position of a tangent.  $s_1$  and  $s_2$  may be brought infinitely close together, so that the temperature change between  $s_1$  and  $s_2$  is infinitely small, and the tangent to the curve will intersect a line joining the two phases at the point which gives the mean composition of the solid which has separated in cooling through that small range of temperature. Tangents at different points along the curve will indicate the composition of the solid which separates dur-

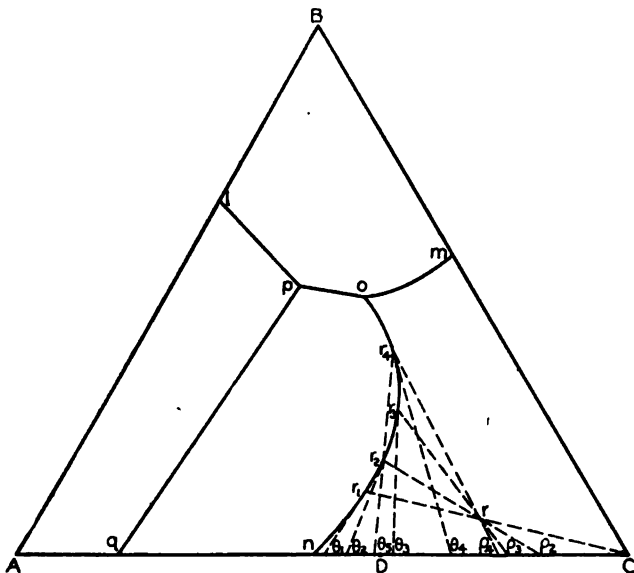


Fig. 4

ing the cooling over the small range of temperature at each point. When a solution is cooled over a considerable part of a boundary curve, as from  $s_1$  to  $s_2$ , the line joining the two points on the curve will intersect the lines joining the composition of the two phases at the point which shows the composition of the crystal mass which separated during that change of temperature, as above discussed.

A tangent drawn at any point between  $s_1$  and  $s_2$  will cut

the line joining DC outside of DC, which indicates, as has been shown in the case of the line  $s_2 s_1 \sigma_4$  that the phase C is disappearing and D is crystallizing. Therefore, it follows, that whenever a tangent to a boundary curve intersects a prolongation of the line joining the composition of the phases coexistent along the curve, one phase will disappear and the other crystallize when solutions are cooled along that boundary curve. It is seen that the tangent to any point on *no* will cut DC on its prolongation beyond D.

It is, however, possible that one phase might disappear and the other crystallize over part of a curve while both would separate over another part of the curve. Consider Fig. 4. D is the compound, instable at its melting-point D, which coexists with solutions in the field *qpon*. From solution  $r_1$  C will crystallize until  $r_1$  is reached on the boundary *no*. A tangent to the curve at  $r_1$  shows that the solid of composition  $\theta_1$  will crystallize in cooling over an infinitely small range of temperature at that point. The intersection of the tangent at  $\theta_1$  is on a prolongation of DC on the side near D. This indicates that C has dissolved and D separated through that small temperature change at  $r_1$ . At  $r_2$  the tangent intersects at  $\theta_2$ . Thus during the cooling at that point C has disappeared and D separated. A line joining  $r_1$  and  $r_2$  will intersect DC somewhere between  $\theta_1$  and  $\theta_2$ . Thus, when the solution  $r_1$  is cooled to  $r_2$  the solid which separates will be indicated by a point lying between  $\theta_1$  and  $\theta_2$ ; that is, C dissolves and D separates during the cooling from  $r_1$  to  $r_2$ . At  $r_3$  the tangent intersects DC at  $\theta_3$ . Now  $\theta_3$  lies between D and C. Therefore, when the solution  $r_3$  is cooled over a small range of temperature at  $r_3$ , both D and C will separate together. Over the small temperature change at  $r_4$  C and D separate together, since the tangent to  $r_4$  intersects DC between D and C at  $\theta_4$ . The line  $r_4 r_2$  intersects at  $\theta_5$ , which shows that over the temperature change from  $r_2$  to  $r_4$  more C has dissolved than has separated; the mean composition change shows a solution of C and a separation of D. Two points on *no* may be selected, an extrapolation on the line between which will intersect at D.

This would show that, during the cooling from the higher to the lower temperature, all the C which had disappeared during the first part of the cooling separated during the second part. Thus the total or mean change has been equivalent to the separation of D which has separated continually from the higher to the lower temperature.

Reverting to Fig. 3, the two cases of solutions in the field  $C_{mon}$  are now to be easily distinguished. The first case, which is typified by solution  $e$ , acts in a manner analogous to those which have previously been discussed. From such a solution the phases which separate during the cooling remain in the solid form. The second case, which is illustrated by solution  $s$ , acts in a different manner. The phase which separated from such a

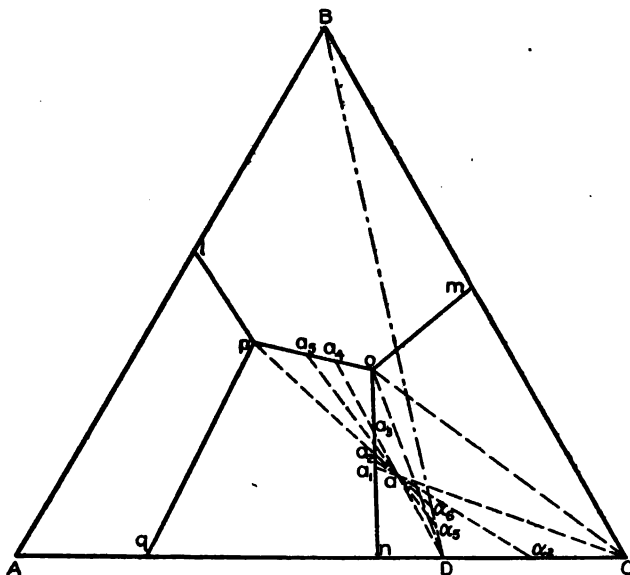


Fig. 5

solution while the crystallization curve remained in the original field will, wholly or in part, disappear while the crystallization curve follows the first boundary curve which is intercepted; in other words, the phase may partly crystallize and partly disappear.

A subdivision of the second case is illustrated by Fig. 5. Since the solution  $a$  lies within the field for pure C, that com-

ponent will be the first to appear as solid when the solution is cooled. As in the former cases the composition of the solution changes along the straight line crystallization curve and hence intercepts the boundary *no* at  $a_1$ . This solution is saturated with respect to both C and D, and hence when  $a_1$  is cooled to  $a_2$  the solid consists of both C and D, the mean composition of which is  $a_2$ . On continued cooling  $a_3$  is reached and the composition of the solid is found to be that of the compound D. During the cooling of the solution *a* through its changes  $a_1$ ,  $a_2$ , to  $a_3$ , the extrapolation to the line joining the composition of the pure phases separating, shows that the mean composition of the crystal mass has been steadily decreasing in its percent of C. Since the solid phase originally consisted of pure C and changes from 100 percent C to that called for by the composition of the compound D, while D and C are supposed to separate together, it must follow that this change means that pure C disappears faster than it crystallizes, which is but saying in other words, that the component C, which has separated in cooling along the curve from *a* to  $a_1$ , has disappeared in cooling from  $a_1$  to  $a_3$ , while the compound D has crystallized. With the solution  $a_3$ , then, there exists in equilibrium only the compound D.

When the solution  $a_3$  is cooled again there seems to be but one of two courses for the crystallization curve. It might follow the boundary curve, as in the preceding cases, to the quintuple point *o*. By this hypothesis the mean composition of the solid in equilibrium with the solution would be given by points along AC, but on the side of D away from C. Such a course, however, is impossible, because there is no mixture of C and D which, by any possible combination, can be made to contain an amount of C less than that required for the composition of D. Therefore, the crystallization curve cannot follow the boundary curve *no* to the quintuple point *o*. That this conclusion is the correct one is evident also from a consideration of the following facts: since C disappears during the cooling from  $a_1$  to  $a_3$ , since there is no more C to so change, and since D is

stable at the temperatures in question, the crystallization curve cannot follow the boundary beyond  $a_3$ . Consequently, on further cooling the crystallization curve takes the only other possible course. D continues to separate, the crystallization curve leaves the boundary, crosses the field  $qpon$ , wherein D is the solid phase, and intercepts the boundary  $op$  at  $a_4$ . In accordance with the principles of equilibrium, the solution  $a_4$  is saturated with respect to B as well as to D. Hence, on cooling the solution, the crystallization curve passes along the boundary  $op$  with a separation of B and D. The mean composition of the solid is given by the points  $a_3$  and  $a_4$ . The latter is that of the solid when the crystallization curve first reaches the quintuple point  $p$ , which is the end of the curve.

In the course of the cooling there have appeared consecutively pure C; C and D; pure D; D and B; and finally D, B and A. It is seen, therefore, that whenever there exists a ternary system which contains a compound instable at its melting-point, solutions can be found whose crystallization curves do not follow the first boundary curve intercepted to its quintuple point, but which may pass into the field for the compound and follow some other boundary to another quintuple point. From a consideration of the diagrams shown as Figs. 1, 2, 3, and 5, it is evident that the crystallization curve can leave the boundary only when there is reached some point from which the line, through the point giving the composition of the original solution, passes also through that which gives the composition of the compound in question. Naturally these considerations apply equally well to binary and ternary compounds.

Solutions with which this condition can be attained lie within a limited field. By an inspection of the diagram in Fig. 4 one can observe that such solutions are possible only within the limits of the triangle  $noD$ . The field  $nomC$  may be divided into three parts by lines from the quintuple point  $o$  to C and to D. For solutions within the triangle  $Com$  the crystallization curve will proceed from C to the boundary  $om$ , while C separates, then follow that boundary to the eutectic  $o$ , while C and B sepa-

rate together. Such a solution is  $e$ , Fig. 3. Obviously, if the solution is on the line  $C$  the crystallization curve will follow that line to  $o$ ,  $C$  separating alone. Within the triangle  $noC$  the crystallization curve will follow a line straight away from  $C$ , with  $C$  separating. It will follow the boundary  $no$  with  $D$  separating and  $C$  redissolving and will end at  $o$ . Such is solution  $s$ , Fig. 3. The triangle  $noD$  incloses that part of the field within which crystallization curves leave the boundary  $no$ , cross the field  $qpon$  and end finally at the eutectic  $p$ .  $C$  will crystallize while the crystallization curve remains in the field  $nomC$ . So long as the crystallization curve follows the boundary curve  $no$ ,  $D$  will separate and  $C$  disappear in a manner similar to those solutions in the triangle  $DoC$ . On leaving the boundary curve  $no$ ,  $D$  separates until another boundary is reached where another phase appears.

A line from  $p$  to  $D$  might divide this field yet again, from the one side of which the crystallization curve will intercept and follow the boundary  $po$ , from the other side of which it will intercept and follow the boundary  $qp$ .

#### General Theoretical Conclusions

In general, there are two classes of boundary curves:

1. Boundary curves along which two phases crystallize together. A tangent drawn at any point on a boundary curve of this class will intersect the line joining the composition of the two phases between its extremities. This class is illustrated by all the boundary curves in Figs. 1 and 2; and in Fig. 3 by the boundary curves  $om$ ,  $lp$ ,  $op$  and  $pq$ .

2. Boundary curves along which one phase crystallizes while the other disappears. A tangent drawn at any point on a boundary curve of this class will intersect a prolongation of the line joining the composition of the two phases. This class is illustrated by the boundary curve  $on$  in Fig. 3 and  $on$  in Fig. 4. According to the composition of the initial solution Class 2 will be divided yet again into two parts: (a) The solution is so concentrated with respect to the changing phase that it will not all disappear before the quintuple point is reached, and hence the



crystallization curve will follow the boundary curve to that quintuple point. This division is illustrated by solution *s*, Fig. 3. (*b*) The concentration of solutions, with respect to the changing phase, is so low that it disappears before the quintuple point is reached by the crystallization curve, which then leaves the boundary and crosses the field of the separating phase.

A boundary curve may be included wholly in one class or may be partly in one and partly in the other. If the tangents over one part of the curve obey the condition of Class 1, then along that part of the boundary curve both phases will separate. If the tangents over part of the curve obey the condition of Class 2, then along that part of the curve one phase will separate and the other dissolve.

A recognition of the above facts is of considerable importance in the study of ternary systems. If one is locating the boundary curves and quintuple points by the discontinuities in, say, a time curve of cooling, it is quite necessary to know the cause of each break. Ordinarily one starts with an unsaturated solution so that the first break is at the freezing-point of the first phase to separate, the second break, then, is at the intersection of the boundary curve, and the third break, in such a case, is at the quintuple point. In Fig. 5 it is seen that solution *a* would show five breaks, at the freezing-point *a*, *a*<sub>1</sub>, *a*<sub>3</sub>, *a*<sub>4</sub> and *p*, the fifth of which would be at the quintuple point.

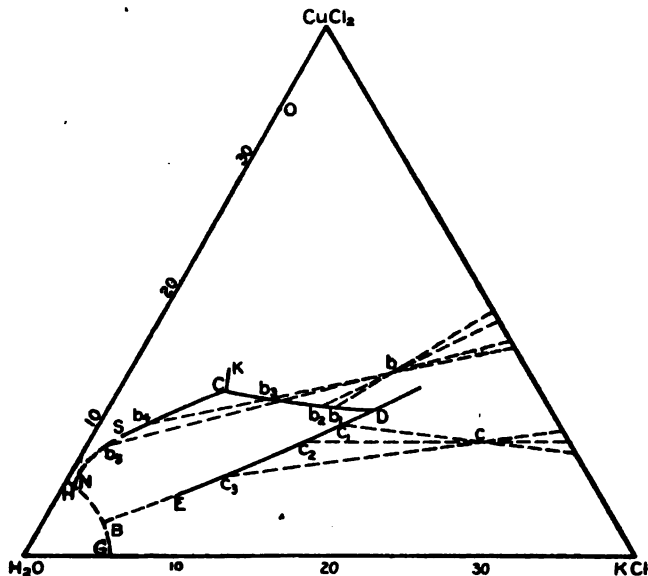
From any of the solutions discussed the amount of solid which separates, between any two temperatures, may be computed by the methods given on page 259. The ratios there discussed will find analogies in the case of any other solution.

### III. APPLICATION TO PREVIOUSLY PUBLISHED DATA

The principles discussed in the foregoing paragraphs may be applied to those cases of equilibrium between three components which have been so thoroughly studied that it is possible to plot the data in the form of the triangular diagram. It then becomes possible to predict the course of the crystallization curves from some initial solutions and to show the composition of solid and solution throughout their extent. When complete

data are not at hand, as, indeed, is usually the case, the crystallization curves may be drawn over those fields and boundaries that are known. If the direction of a boundary is questionable, the crystallization curve may be tentatively drawn by arbitrarily assuming the form of the unknown boundary. In such a case the experimentally determined course of the crystallization curve may become a means of determining the path of the boundary within certain limits.

1. *The System Copper Chloride, Potassium Chloride and Water.*—The first diagram to be considered is the system  $\text{CuCl}_2$ ,  $\text{KCl}$  and  $\text{H}_2\text{O}$ , the data for which were determined by Meyerhoffer.<sup>1</sup> Fig. 6 is taken with some modification from another



**Fig. 6**

source.\* Fig. 6a supplements Fig. 6, giving some points which could not conveniently be included in the other on account of the scale.

The meaning of the boundaries and fixed points becomes

<sup>1</sup> Zeit. phys. Chem. 3, 336 (1889) ; 5, 97 (1890).

<sup>2</sup> Bancroft. The Phase Rule, p. 176 (1897).

clear when one recalls that within the field HNCK, the limit of which is indeterminate, the solid phase  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  is in equilibrium with solution and vapor; in the field XHNG, ice is solid; in GBEF, KCl is solid with the extension of F undetermined; KCDF is the field for  $\text{CuCl}_2 \cdot \text{KCl}$ ; and NBCD is that for the ternary compound,  $\text{CuCl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}$ . The points X, Y and Z represent the compositions of the pure components  $\text{H}_2\text{O}$ ,  $\text{CuCl}_2$  and KCl; the point O gives the composition of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ; P,  $\text{CuCl}_2 \cdot \text{KCl}$ ; and Q,  $\text{CuCl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}$ .

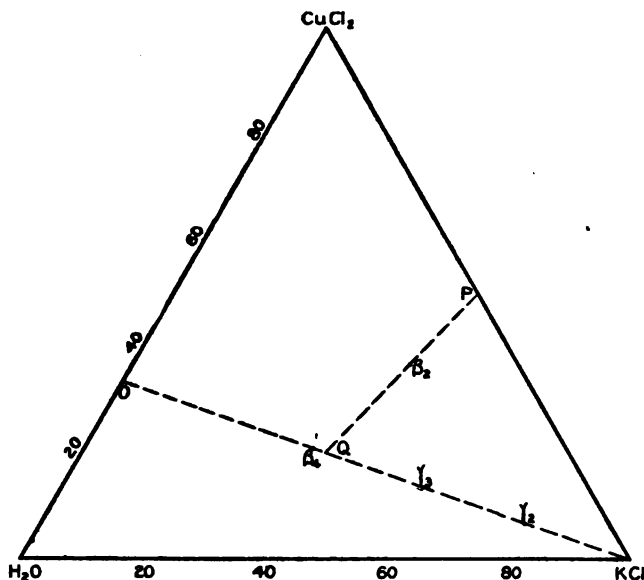


Fig. 6a

The temperature of H,<sup>1</sup> the eutectic for ice and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , is  $-23^\circ$ . G is the eutectic<sup>2</sup> for ice and KCl, at  $-11.14^\circ$ . C is at  $56^\circ$ ; D at  $92^\circ$ ; E at  $39^\circ$ ; and S at  $0^\circ$ .

From these data one can predict the crystallization curves of many solutions. On cooling the solution whose composition is given by c, pure KCl will separate as a white solid. From the diagram one sees that the initial temperature must be near the boiling-

<sup>1</sup> de Coppet. Ann. Chim. Phys. (4) 23, 386 (1871).

<sup>2</sup> Guthrie. Phil. Mag. [4] 49, 269 (1875).

point of the solution. The crystallization curve follows the straight line law and meets the boundary DE at  $c_1$ , the temperature of which is somewhat below  $92^\circ$ . Since tangents to that part of the curve ED intersect on the prolongation of KCl-Q beyond Q, KCl will dissolve and  $\text{CuCl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}$  separate, while the solution changes concentration along the boundary DEB. The points  $c_1$  and  $c_3$  are in equilibrium with crystal masses which are given by extrapolation through  $c$  to the line joining the points representing the composition of the pure phases in the separated mass, viz. KCl-Q. The points so found are  $\gamma_2$  and  $\gamma_3$ . When cooled still lower the crystallization curve will follow the boundary to E, whence it will extend to the ternary eutectic which, though undetermined, is probably, as indicated, at B, where ice appears.

In the case of solution  $b$  the peculiarity noted in Fig. 5 is observed. Since  $b$  is in the field wherein  $\text{CuCl}_2 \cdot \text{KCl}$  is solid phase, that compound will separate first, in the form of red crystals. The composition is given by P. When the crystallization curve intercepts the boundary CD the blue ternary compound  $\text{CuCl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}$  will appear together with the red binary compound. It is seen from the diagram that tangents to the boundary curve CD will intersect the prolongation of PQ. Therefore, on following the crystallization curve from  $b$  to  $b_1$ , P will separate pure. Along the boundary from  $b_1$  to  $b_2$  and  $b_3$ , Q will separate and P disappear. The solid will consist of a mixture of P and Q given by points on the line PQ, as  $\beta_1$ . When the point  $b_3$  is reached, the composition of the solid will be that of Q alone. Thus P will continually disappear and Q separate in passing from  $b_1$  to  $b_3$ .

From a reference to the discussion of Fig. 5 it appears that the crystallization curve from  $b_3$  will cross the field, wherein the blue ternary compound is solid phase, and intercept another boundary CS at  $b_4$ . During the cooling the solid phase will consist of Q. When the temperature becomes lower than  $b_4$ , a new phase will appear, the green  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ . Since tangents to the curve CS will intersect the line QO between its extremities, the blue  $\text{CuCl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}$  will separate with  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$



The compositions of the phases are given by the points :

I for  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$   
 J for  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$   
 P for  $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$   
 Q for  $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ .<sup>1</sup>

The temperatures of the eutectics are

G	—1.2°	H	—6.0°	A	—4.5°	B	—3.0°
C	47.2°	K	48.2°	D	72.0°	E	92.0°.

From the solution  $a$ ,  $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  will crystallize, since the solution starts in the field for that compound. The crystallization curve will follow the straight line  $aa_1$  until  $a_1$  is reached. Since tangents to DE intersect a prolongation of QP, which lies outside the figure, the compound mentioned will disappear and  $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , whose composition is indicated by  $P^1$ , will separate during the cooling from  $a_1$  to  $a_2$ . At  $a_2$  the extrapolation passes back through  $P^1$ . Accordingly, the crystallization curve will cross the field for  $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  and intercept the boundary BC at  $a_3$ . On further cooling the last mentioned ternary compound crystallizes with  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , since tangents to the curve BC intersect  $JP^1$  between  $J^1$  and  $P^1$ . The composition of the solid which separates is given by points on  $JP^1$ . The crystallization curve follows the boundary curve to the quintuple point B, where  $\text{K}_2\text{SO}_4$  appears. The solution will remain at the temperature of B, — 3°, until all the  $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  has separated. The crystallization curve will then follow the boundary curve BA to A, — 4.15°. At the latter temperature ice appears and the whole becomes solid.

From the solution  $b$ , there will first separate  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  whose composition is given by  $I^1$ , and the crystallization curve intercepts the boundary for  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  at  $b_1$ . Tangents to the curve CK intersect a prolongation of  $IJ^1$ .

<sup>1</sup> The whole triangular diagram is too large to show on a cut, so that the part including the points I, J, P, and Q is left out of Fig. 7. I and J lie on the left side of the triangle; P and Q lie on a line from the  $\text{H}_2\text{O}$  apex through the centre of the triangle.

From  $b_1$  to  $b_2$   $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  will disappear and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  crystallize. At  $b_2$  the mean composition of the solid phase is, by extrapolation,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , so that the curve will leave the boundary at  $b_2$  cross the field to  $b_3$ , while  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  will separate. Tangents to the curve  $BC$  intersect  $JP^1$  between  $J^1$  and  $P^1$ . Therefore, from  $b_3$   $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  will crystallize with the  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ . The crystallization curve will follow the boundary curve  $CB$  to  $B$ , where  $\text{K}_2\text{SO}_4$  will appear with the two compounds which separated along  $CB$ . The composition of the solid which is in equilibrium with any solution along  $b_2B$ , is given by some point on  $JP^1$ . When all the  $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  has separated, the crystallization curve will follow the boundary  $BA$  to  $A$ , where the solution goes solid with the appearance of ice in the crystal mass.

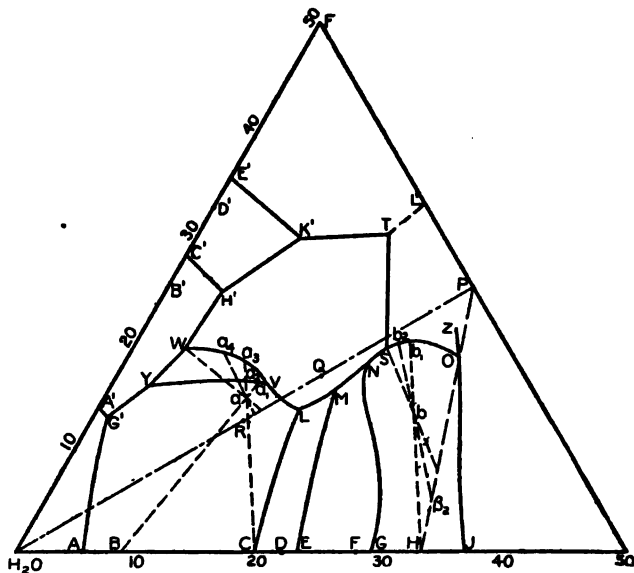


Fig. 8

3. *The System Ferric Chloride, Hydrochloric Acid and Water.*—The system  $\text{FeCl}_3, \text{HCl}, \text{H}_2\text{O}$  is shown in Fig. 8. The data are from the well known work of Roozeboom<sup>2</sup> and Rooze-

<sup>1</sup> See note on preceding page.

<sup>2</sup> Zeit. phys. Chem. 10, 417 (1892).

boom and Schreinemakers.<sup>1</sup> The diagram is taken from the Phase Rule.<sup>2</sup>

Although the diagram is somewhat replete with boundaries and quintuple points, there are but two crystallization curves which are of special interest from the point of view of the present paper. The data necessary for an understanding of the figure are given below :

Fields	
A'GA	solid phase is $H_2O$
A'GH'E'	" " " $HCl.3H_2O$
C'H'K'E'	" " " $HCl.2H_2O$
E'K'TL'	" " " $HCl.H_2O$
AGLC	" " " $Fe_2Cl_6.12H_2O$
CLME	" " " $Fe_2Cl_6.7H_2O$
EMNG	" " " $Fe_2Cl_6.5H_2O$
GNSJ	" " " $Fe_2Cl_6.4H_2O$
JOL	" " " $Fe_2Cl_6$
YWV	" " " $Fe_2Cl_6.2HCl.12H_2O$
WVLMTK'	" " " $Fe_2Cl_6.2HCl.8H_2O$
L'TSZ	" " " $Fe_2Cl_6.2HCl.4H_2O$

Composition of the solid phases is given by

P	for $Fe_2Cl_6.2HCl.4H_2O$
Q	" $Fe_2Cl_6.2HCl.8H_2O$
R	" $Fe_2Cl_6.2HCl.12H_2O$
B'	" $HCl.3H_2O$
D'	" $HCl.2H_2O$
F'	" $HCl.H_2O$
B	" $Fe_2Cl_6.12H_2O$
D	" $Fe_2Cl_6.7H_2O$
F	" $Fe_2Cl_6.5H_2O$
H	" $Fe_2Cl_6.4H_2O$

Temperature of quintuple points :

G'	$-100^\circ$	M	$-7.3^\circ$
Y	$-60^\circ$	N	$-16.0^\circ$
W	$-40^\circ$	S	$-27.5^\circ$
V	$-13^\circ$	O	$+29.0^\circ$
L	$-7.5^\circ$	T	$-65.0^\circ$

Within any field wherein the solid phase is stable at its melting-point the simple case, which is exemplified in Fig. 1, is

<sup>1</sup> Zeit. phys. Chem. 15, 588 (1894).

<sup>2</sup> Bancroft. The Phase Rule, p. 220 (1897).



illustrated. The crystallization curve will proceed along the line connecting the initial solution with the point giving the composition of the solid phase and follow the first boundary to the quintuple point. Such a condition exists in every field, but one, in the diagram. In case the quintuple point that is first reached is not the minimum quintuple point, the solution will remain at the temperature of the quintuple point first reached until one phase has entirely disappeared. The crystallization curve will then follow the boundary to the next quintuple point, and so on. Or, the solution may become solid at the first quintuple point reached, depending upon the initial concentration of the solution.

From the solution *b*, Fig. 8, in the field GNSOJ there will separate pure  $\text{Fe}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$  until the boundary OS is reached, along which the solid separated consists of two phases,  $\text{Fe}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$  and the ternary compound  $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 4\text{H}_2\text{O}$ . PH is the line which joins the points giving the composition of the pure phases mentioned, on which is found by extrapolation the mean percentage composition of the solid separated. Both phases separate together, since tangents to the boundary intersect this line between P and H. The solution will remain at the temperature of S,  $-27.5^\circ$ , where  $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 8\text{H}_2\text{O}$  will appear, until all the  $\text{Fe}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$  has disappeared. The crystallization curve will then follow the boundary ST to T, at  $-65^\circ$ , where  $\text{H}_2\text{O}$  will appear.

Only one compound, for which the complete field is known, is instable at its melting-point. This compound is  $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 12\text{H}_2\text{O}$ , coexistent with solution within the field YVW. The point R indicates its composition. From the solution *a*, taken as a starting point,  $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$  will first separate, while the solution changes along the crystallization curve Ba to *a*. From *a*  $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$  and  $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 12\text{H}_2\text{O}$  together comprise the solid; the former will disappear and the latter crystallize until a point on the boundary YV is reached, from which the extrapolation through *a* will also pass through R<sup>1</sup>. The solid in

<sup>1</sup> By an oversight this line in the diagram was not drawn to pass through R.

equilibrium with this solution, which is  $a_2$ , is pure R, i. e.,  $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 12\text{H}_2\text{O}$ . As in the previous analogous cases the crystallization curve will leave the boundary and cross the field YWV to  $a_3$ . From  $a_3$  the crystallization curve will follow the boundary VW with  $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 8\text{H}_2\text{O}$  and  $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 12\text{H}_2\text{O}$ , separating together until  $a_4$  is reached. Tangents to the curve VW between  $a_3$  and  $a_4$  will intersect RQ between R and Q. Hence, over this portion of the boundary curve the phases will separate together. Tangents to VW between  $a_4$  and W will intersect RQ beyond Q. Between  $a_4$  and W, therefore, R, or  $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 8\text{H}_2\text{O}$ , will redissolve and Q, or  $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 12\text{H}_2\text{O}$ , will continue to separate. The solution will remain at the temperature of W until all the  $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 12\text{H}_2\text{O}$  has disappeared. The crystallization curve will then follow WY to Y with a separation of  $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 8\text{H}_2\text{O}$  and  $\text{HCl} \cdot 2\text{H}_2\text{O}$ . The solution will remain at the temperature of Y until all the  $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 8\text{H}_2\text{O}$  has disappeared. The crystallization curve will then follow the boundary YG', to G' with a separation of  $\text{HCl} \cdot 2\text{H}_2\text{O}$  and  $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ . At G' ice appears and all goes solid.

The amount of the solid, which separates from any solution discussed, in cooling between two temperatures may be computed by the method discussed on p. 259.  $\text{CuCl}_2 \cdot \text{KCl}$  will separate from the solution  $b$ , Fig. 6, when the solution is cooled from  $b$  to  $b_1$ . The percentage of the initial solution  $b$  which will separate as  $\text{CuCl}_2 \cdot \text{KCl}$  may be computed from the ratio

$$\frac{b b_1}{b p},$$

which numerically is equivalent to  $13/210$  or 6.2 percent. The percentage composition of  $b$  is:  $\text{H}_2\text{O}$ , 70.0;  $\text{KCl}$ , 16.66;  $\text{CuCl}_2$ , 13.34; total, 100.00. For simplicity the composition of the solution will be expressed in kilograms;  $\text{H}_2\text{O}$ , 70.0 kg;  $\text{KCl}$ , 16.66 kg;  $\text{CuCl}_2$ , 13.34 kg; total, 100 kg. Then 6.2 kg will separate as  $\text{CuCl}_2 \cdot \text{KCl}$ . Since  $\text{CuCl}_2 \cdot \text{KCl}$  is composed of equal molecular parts of  $\text{CuCl}_2$  and  $\text{KCl}$  the new solution  $b_1$  will be made up of  $\text{H}_2\text{O}$ , 70.0 kg;  $\text{KCl}$ ,  $16.66 - 3.1 = 13.56$  kg;  $\text{CuCl}_2$ ,  $13.34 - 3.1 = 10.24$  kg. The percentage composition, then, is

$\text{H}_2\text{O}$ , 74.7;  $\text{KCl}$ , 14.4;  $\text{CuCl}_2$ , 10.9. These figures are seen to be verified by the position of  $b_1$  on the diagram.

In the same manner the amount of the solid separated from any solution may be computed. Evidently the proper ratio must be chosen. In each case, however, that ratio is easily found from the diagram.

4. *The System Gold, Cadmium and Tin.* — An interesting study in the application of the laws of crystallization as a means of predicting the course of some boundary curves when not fully known, is to be found in the case of one boundary curve in the diagram of the equilibria between Au, Cd and Sn. The diagram with slight additions was taken from a paper by Shepherd,<sup>1</sup> who recalculated and discussed the data of Heycock and Neville.<sup>2</sup>

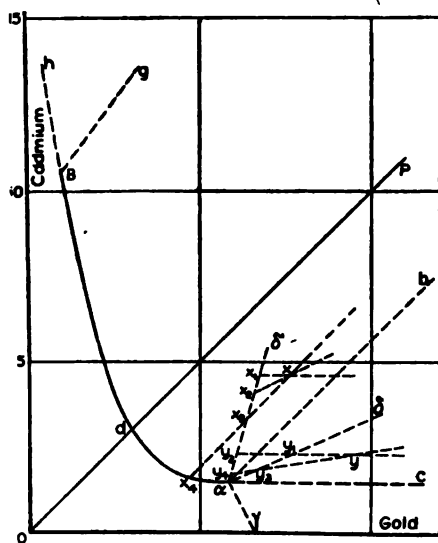


Fig. 9

In Fig. 9, the field to the left of  $\gamma a B h$  contains Sn as solid phase;  $\gamma a \delta$ , etc., Au; and  $\delta a B g$ , AuCd. Therefore,  $a \gamma$  is the boundary curve along which Au and Sn are solid phases;  $a \delta$ ,

<sup>1</sup> Jour. Phys. Chem. 8, 92 (1904).

<sup>2</sup> Jour. Chem. Soc. 59, 936 (1891); 65, 65 (1894).

that of Au and AuCd;  $aB$ , Sn and AuCd;  $Bh$ , AuCd<sub>3</sub> and Sn; and  $Bg$ , AuCd<sub>3</sub> and AuCd. The quintuple points are  $\alpha$  and  $\beta$ , the temperatures of which are respectively  $18.74^\circ\text{C}$  and  $20.9^\circ\text{C}$  below the melting-point of Sn, which is  $232^\circ\text{C}$ . A maximum exists at  $d'$ , which is  $13.88^\circ\text{C}$  below the melting point of Sn.

The exact position of the boundary  $a\delta$  is uncertain. It may be, in general, either  $a\delta$  or  $a\delta'$ . In the former case its direction is such that one would say that the binary compound AuCd is stable at its melting-point, and the point representing that composition lies, on a triangular diagram, in the field in which it is in equilibrium with solution. In the latter case the direction of  $a\delta'$  is such that the composition of AuCd, which lies on OP, is not within its field, and hence this compound is instable at its melting-point.

Since the diagram is plotted in parts per hundred of tin, the crystallization curve in any field will lie parallel to a line joining the origin and the composition of the phase separating. For the field in which Au is the solid phase, viz.,  $\gamma a\delta$ , the crystallization curve will extend in a direction parallel to the Sn-Au axis; for the field in which Cd is solid it will extend parallel to the Sn-Cd axis; and so for the other fields. For the Sn field obviously the crystallization curve extends to the origin O.

In order to predict which of the two courses the AuCd-Au boundary should take it is necessary to consider the course of crystallization curves which extend from some one initial solution to each possible boundary. The composition of the solid phases and of the solutions will then afford the data from which the desired direction may be predicted.

Suppose that the boundary is the line  $a\delta'$ . Then a solution whose composition in the diagram is given by  $x$  lies in the field within which Au is the solid phase. When cooled the solution will follow the crystallization curve from  $x$  to  $x_1$ , with Au precipitating. From  $x_1$  the assumed boundary  $a\delta'$  will be followed to  $x_2$  and  $x_3$ , while AuCd will separate and Au disappear. When the crystallization curve reaches  $x_3$  the composition of the solid which has separated is AuCd, since  $xx_3$  is parallel to OP.

On cooling to lower temperatures Au will continue to separate, the crystallization curve will cross the field to  $x_4$ , where it intercepts the AuCd-Sn boundary, follow that boundary with separation of AuCd and Sn until the ternary eutectic is reached at  $a$ , where Au appears. If a solution follows the above-mentioned changes in the order given, then  $a\delta'$  is the position of the boundary. If, however,  $a\delta$  were the position of the boundary, the crystallization curve would extend from  $x$  to  $x_4$  with separation first of AuCd, then follow  $\beta a$  to  $a$  with separation of Sn and AuCd, and finally end at  $a$ , where Au appears. The various concentration changes will be in the order mentioned, and if thus found in fact will indicate that the boundary curve lies at  $a\delta'$ .

A solution  $y$  within the field  $bac$  will in either event, viz., whether the boundary is  $a\delta$  or  $a\delta'$ , show crystals of the same kind and order of separation. Thus, Au will crystallize and the crystallization curve will break either at  $y_1$ , or  $y_2$ . At either point AuCd and Au will begin to separate together. They will continue to separate together while the crystallization curve will follow the boundary, either  $a\delta$  or  $a\delta'$  until the eutectic  $a$  is reached. At the latter point Sn will crystallize with Au and AuCd. To locate experimentally the boundary between the Au and AuCd fields some solution in the triangular field  $\delta'a\beta$  is the best with which to begin.

### Summary

In the preceding paragraphs the attempt has been made to elucidate the laws of crystallization in three-component systems by a discussion of the following points:

1. The fundamental principles of crystallization in three-component systems were discussed with the aid of the triangular diagram.
2. The crystallization curve for any initial solution was defined as the locus of the points which represent the compositions of the solutions formed on cooling a given solution from any given temperature to the quintuple point at which it becomes solid, under the assumption that no phase is removed during the

cooling. The course of the crystallization curve was shown to be a straight line in a field, otherwise to follow the course of boundary curves.

3. The composition of the solid which separated between any two temperatures was found on extrapolation of the line joining the composition of the solutions at those temperatures to its intersection with the line joining the composition of the phases which separate.

4. The amount of the solid which separates between two temperatures was shown to be capable of easy computation. Two types of ternary systems were discussed: one, in which no compound exists; the other, in which compounds exist, which might be stable or instable at their respective melting-points.

6. Two classes of boundary curves were discussed. The first class comprises those boundary curves along which the phases separate together. The second class comprises those boundary curves along which one phase will disappear while the other will crystallize.

7. As a subdivision of the second class it was shown that during the cooling of certain solutions the crystallization curve may leave the boundary curve and cross the field to another boundary curve.

8. The laws theoretically discussed were applied to data actually worked out and published. The systems  $\text{CuCl}_2$ ,  $\text{KCl}$ ,  $\text{H}_2\text{O}$ ;  $\text{MgSO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ ;  $\text{Fe}_2\text{Cl}_6$ ,  $\text{HCl}$ ,  $\text{H}_2\text{O}$ ; and  $\text{Au}$ ,  $\text{Sn}$ ,  $\text{Cd}$  were considered. In each case the paths of different crystallization curves were drawn and the compositions of the solids, which would separate, predicted.

In a later paper will be discussed systems in which there may exist solid solutions and in which two liquid layers may be present.

Sincere thanks are extended to Professor Bancroft who suggested the undertaking and through whose kind assistance it has been carried out.

*Cornell University,  
Ithaca, N. Y.*

## NEW BOOKS

**Einteilung der Elemente.** By *Henri Moissan*. *Autorisierte deutsche Ausgabe von Th. Zettel.* 17 × 25 cm; pp. 58. Berlin: M. Krayn, 1904. Price: paper, 2 marks. — After a discussion of the development of our conception of an element, the author discusses a number of suggested classifications of the metals, including those of Regnault, Berzelius, Dumas, Frémy, Maquet, and Mendelejeff, together with the modifications of the Periodic Law suggested after the discovery of the inert gases. Moissan himself arranges the elements in the following groups, which are based on chemical and physical properties rather than on atomic weights:

Hydrogen, helium.

Fluorine, chlorine, bromine, iodine.

Oxygen, sulphur, selenium, tellurium.

Neon, argon, krypton, xenon.

Nitrogen, phosphorus, arsenic, antimony, bismuth, vanadium, columbium, tantalum.

Boron.

Carbon.

Silicon, titanium, zirconium, germanium, tin.

Cæsium, rubidium, potassium, ammonium, sodium, lithium.

Calcium, strontium, barium, radium.

Rare earths, thorium.

Beryllium, magnesium, zinc, cadmium.

Aluminum, gallium, indium.

Cobalt, nickel, iron, manganese, chromium, molybdenum, tungsten, uranium.

Thallium, lead.

Copper, mercury.

Silver.

Gold.

Osmium, ruthenium, platinum, palladium, iridium, rhodium.

During the last thirty-five years the tendency has been to arrange the elements in an order depending on the atomic weights and then to try and prove that the groups thus formed are natural groups. Without saying so explicitly, Moissan's aim is to determine experimentally what elements belong together in groups, leaving to the future the task of arranging these groups with reference to one another and to the atomic weights.

Of special interest are Moissan's remarks on the divisibility of the elements. To Moissan the interconversion of the different members of a single group is a problem of to-day, not one of the remote future.

*Wilder D. Bancroft*

**Elements of Inorganic Chemistry.** By *Harry C. Jones*. 13 × 19 cm; pp. xiii + 343. New York: The Macmillan Company, 1903. Price: bound,

\$7.25. — This is essentially an edition in little of the same author's "Principles of Inorganic Chemistry", already noticed in this Journal (7, 469); and what was there said of the larger work applies with modifications to this one also. There has been some transposition of chapters; a good deal of the more difficult matter has been cut out; and experiments and problems have been added, so as to adapt this book to the uses of a laboratory manual as well as of a text for reading; but in its general lines it is on the same model as its predecessor.

It need hardly be said, then, that the guiding idea of the work is to be found in the theory of electrolytic dissociation. This theory is cleverly introduced quite early in the book to explain the peculiar properties of the hydrogen of acids as compared with those of the same element in other compounds, and throughout the work it is often very happily applied. It is in fact in the text that the main strength of the book lies, for in the course of experiments we do not find any marked departure from conventional lines, except that the directions call for an equipment and a dexterity on the part of the student which the actual beginner rarely possesses; for those who have already had a little laboratory practice, and especially where the laboratory classes are small enough to allow of careful supervision, the course would probably prove satisfactory.

Minor errors in the text can be found if desired; in fact, several of those to which attention was called in the parent volume, have appeared again in the offspring. At the same time, the book will be of service to the many teachers who are now introducing the theory of electrolytic dissociation into elementary instruction; and it can be commended to all such, as well as to all others, as one of the most interesting of recent elementary texts in English.

A. P. Saunders

**Ausgewählte Methoden der analytischen Chemie.** By A. Classen. Zweiter Band. Unter Mitwirkung von H. Cloeren. 15 X 23 cm; pp. xvi + 831. Braunschweig: F. Vieweg und Sohn, 1903. Price: bound, 20 marks. — This second volume of Classen's comprehensive work supplements the first one, and completes the treatment of essentially the whole field of analytical chemistry. The first volume, reviewed in a previous issue, dealt with metals; the present one deals with the non-metals. Oxygen, ozone; hydrogen and its oxides, including the analysis of mineral waters; sulphur, the halogens, nitrogen and its explosive compounds, including smokeless powder; the noble gases, as well as phosphorus, boron, silicon and compounds of carbon, both organic and inorganic, are all discussed. The treatment includes gas volumetric methods as well as gravimetric and liquid volumetric analysis, and the directions are given carefully and intelligently.

It is pleasing to the American to see that methods devised in this country have received a more hearty recognition than is usual in foreign publications. For example, J. Lawrence Smith's method of determining the alkali in silicates is given in detail with strong commendation.

One regrets that this last volume contains no table of atomic weights or stoichiometrical constants, especially since the inadequate table given in the first volume had to be supplemented by a subsequent separate leaflet based upon the international atomic weights. Nevertheless, in view of the wide acceptance



of Küster's convenient little book of tables and other similar books, this lack is not a serious one. The present volume even more perhaps than its predecessor, is one which should find a place in the working library of every analytical chemist.

T. W. Richards

*Propagation de L'Électricité. Histoire et Théorie. By Marcel Brillouin. 16 × 25 cm; pp. vi + 395. Paris: A. Hermann, 1904. Price: paper, 15 francs.* — This is a noteworthy book, and the reviewer regrets that there is not space here to enter into it in detail. Much greater strain is put on the mathematical resources of the reader than was necessary in the other larger books on electricity which have recently been issued in Paris, though the author endeavors to supply such of the less familiar properties of Bessel functions and spherical harmonics as bear upon his discussions. The historical criticism is splendidly done. The author is intimately acquainted with the original sources, and his criticism is throughout characterized by terseness, acumen, and impartiality. In this respect it differs refreshingly from the usual historical summaries, with their marked nationalistic taint.

The book falls naturally into two parts, in the first of which the phenomenon of conduction, as it grew out of the labors of Ohm, Kirchhoff, Clausius, Joule, and Kelvin, is developed into its remotest consequences. In the second part the phenomenon of induction, beginning with the researches of Faraday, Lenz, Neumann, Helmholtz, and Kelvin, and continuing with Maxwell and Hertz, is taken up with similar fulness. In the first part, the difficult conditions met with at the electrodes, the conduction of cylinders and cables, and the electrostatic field accompanying conduction, are the main features. In the second part, after the usual phenomena encountered in connection with alternating currents have been set forth, the oscillating electromagnetic field is exhaustively treated, at least in so far as the oscillations generated by the Hertzian exciter, by a conducting sphere, and by a conducting ellipsoid of revolution, are concerned. Tables to facilitate the numerical calculations are appended.

C. Barus

*The Electrolysis of Water. Processes and Applications. By Viktor Engelhardt. Authorized English Translation by Joseph W. Richards. 15 × 23 cm; pp. x + 140. Easton: The Chemical Publishing Company, 1904. Price: paper, \$1.00; cloth, \$1.25.* — The book itself has already been noticed when the German edition first appeared. It is a great pleasure to call attention to the first of a series of English translations of these useful monographs. The quality of the translation may be gathered from the following extract: "About the middle of 1880 the industrial application of the electrolytic decomposition of water began to be taken up and was commenced with the use of porous diaphragms."

Wilder D. Bancroft

*Über die Lösungen. By W. Herz. Einführung in die Theorie der Lösungen, die Dissoziationstheorie und das Massenwirkungsgesetz. 15 × 23 cm; pp. 50. Leipzig: Veit und Comp., 1903. Price: paper, 1.40 marks.* — This little volume, like the larger one by Cohen, is the result of a series of lectures to physicians and teachers. As there are only fifty pages in all, the treatment is necessarily more brief and more elementary than in Cohen's book. The

pamphlet, for it is nothing more, is of value to any one who wishes to learn in one evening what the electrolytic dissociation theory is.

*Wilder D. Bancroft*

**La Théorie gyrostatique de la Lumière.** By *H. Chipart*. 16 × 25 cm; pp. 192. Paris: *Gauthier-Villars*, 1904. Price: paper, 6.50 francs. — This book is a determined and powerful effort to revive the elastic theory of light. It is well known that Fresnelian optics broke down eventually, because of the difficulty of obtaining an unimpeachable account of transversality and of the fate of the longitudinal wave. The questions were threshed out at length by Lord Kelvin in his Baltimore lectures. Later Kelvin took up the subject afresh, and produced the gyroscopic theory, which is the basis of the book before us. As the author tersely puts it: " . . . les équations de Fresnel exprimaient des rapports vrais: qu'on y remplace le mot 'vibration' par le mot 'rotation', et le mot 'force' par le mot 'couple', on obtiendra les équations de la théorie gyrostatique."

The reader, to enjoy the book, must be thoroughly versed in solid geometry and in the dynamics or elastics of continuous media, for little relevant explanation is given. The notation of Grassmann for vectors and vortices is used throughout. As a result of this terseness, an extensive amount of optical territory is re-surveyed by the aid of the modified elastic apparatus specified, and there can be no doubt that the book is a noteworthy achievement. One may note in passing that the electromagnetic theory is not as alone in the field as is commonly supposed.

*C. Barus*

**Grundriss einer Geschichte der Naturwissenschaften, zugleich eine Einführung in das Studium der Grundlegenden naturwissenschaftlichen Literatur.** By *Friedrich Dannemann*. II. Band. *Die Entwicklung der Naturwissenschaften*. Zweite, neu Bearbeitete Auflage. 15 × 23 cm; pp. 450. Leipzig: *Wilhelm Engelmann*, 1903. Price: paper, 10; bound, 11 marks. — The first edition of this book has already been noticed in this Journal (4, 213). The present edition claims to be "in many respects enlarged and improved." The book is just what it aims at being—a connected history in outline of the entire field of the natural sciences, with mechanics and mathematics; and it is an excellent book, informing for the layman; stimulating to the scientific worker, fascinating readings for any one with an intelligent interest in scientific thought.

The early appearance of a second edition shows that the work has reached a wide audience among readers of German; a translation into English would form a notable addition to what one may call the general literature of science in our language, and would place a delightful book within the reach of many a reader to whom it would afford a widened view and a clearer sense of science as a whole.

*A. P. Saunders*

**Recherches sur les Substances radioactives.** By *Skłodowska Curie*. Deuxième Édition, revue et corrigée. 16 × 25 cm; pp. 155. Paris: *Gauthier-Villars*, 1904. Price: paper, 5 francs. — This is Mme. Curie's doctor thesis and it will probably be a long while before so important a piece of work will be presented by any one studying for an advanced degree. The final conclusions will interest every one and are therefore given in full.

"The most recent investigations favor the hypothesis of an atomic transformation of radium. This hypothesis was advanced at the very beginning of the experiments on radio-activity and has been frankly adopted by Mr. Rutherford, who has believed that the emanation from radium is a material gas and one of the decomposition products of the radium atom. The recent experiments of Messrs. Ramsay and Soddy tend to prove that the emanation is an instable gas which breaks down with the formation of helium. Furthermore, the continuous outflow of heat from the radium can hardly be explained by an ordinary chemical reaction while it might perhaps have its origin in a transformation of the atom.

"Remember also that the new radio-active substances are found always in uranium minerals, and that we have sought in vain for radium in the barium salts of commerce. The presence of radium appears therefore to be connected with that of uranium. The uranium minerals contain argon and helium also, and this coincidence is probably not an accidental one. The simultaneous presence of these different substances in the same minerals makes one suspect that the presence of one is necessary for the formation of the others.

"It is necessary however to state that there may be a different explanation for the facts which have been cited in favor of the view of an atomic transformation of radium. Instead of assuming that the atom of radium changes, one may assume that this atom is really stable, but that it acts on the surrounding medium (neighboring material atoms or the ether) in such a way as to cause atomic changes. This hypothesis leads us also to assume the transmutation of the elements, but radium would not then be considered as an element which is being destroyed."

Wilder D. Bancroft

**Untersuchungen über die radioaktiven Substanzen.** By Mme. S. Curie. *Übersetzt und mit Litteratur-Ergänzungen versehen von W. Kaufmann.* (Die Wissenschaft, Heft I.) 14 X 22 cm; pp. viii + 132. Braunschweig: Friedr. Vieweg und Sohn, 1904. Price: paper, 3; bound, 3.80 marks.—This is a German translation of Mme. Curie's thesis (preceding review). The translator has appended a bibliography coming down to October, 1903.

Wilder D. Bancroft

**First Course in Microchemical Analysis.** By Carl Gustav Hinrichs. 15 X 22 cm; pp. 145. St. Louis: Carl Gustav Hinrichs. New York and Leipzig: Lemcke and Buechner. London: H. Grevel and Co. Paris: H. Le Soudier, 1904.—This little book, called by the author a "First Course" in Microchemical Analysis, is evidently intended to supplement certain lectures and class-room conferences, for it is difficult to conceive how it could be used independently as a laboratory manual in laboratories other than those of the authors, where it doubtless serves its purpose. It is greatly to be regretted that the subject-matter has not been arranged and presented in a manner which would permit of the use of the book elsewhere, since valuable new separations are given and order and system has been brought about in the chaos of microchemical methods of analysis.

The usefulness of the book is still further hampered because of the fact that no formulas are given for either reagents or products of reactions nor is

there a single equation indicated. This is all the more remarkable, since most of our microchemical tests are based upon exceptionally interesting and instructive chemical reactions.

In place of formulas the author has introduced a system of his own. The coining of the terms Calcoids for members of the group Ca, Sr, Ba, and Kaloids for  $\text{NH}_4$ , K, Rb, Cs, may be passed without comment, but few, if any, chemists will agree that an alum is — "in ordinary chemical symbols KaApS-ate, hydrated," (page 95), or that such expressions as the following are warranted or justifiable: AgN-ate, NaN-ate, for silver nitrate, sodium nitrate; NaIo-ide, sodium iodide; HS-ate, sulphuric acid; HN-ate, nitric acid; MgAmP-ate,  $\text{PbCl-ide}$ ,  $\text{CuHg}^{\text{te}}\text{S}^{\circ}\text{Cy-ate}$ , etc.

Perhaps this footnote on page 85 may explain many of the peculiar features of the book, as well as that to which the note specifically refers: "We did not find time to reconstruct these figures to a uniform scale and position".

*E. L. Chamot*

## REVIEWS

*The object of this department of the Journal is to issue, as promptly as possible critical digests of all Journal articles that bear upon any phase of Physical Chemistry*

### General

The deduction of the absolute temperature from the normal thermometer.  
*H. Pellat. Comptes rendus, 136, 809 (1903).* — It is customary to take the absolute temperature as

$$T = \frac{t}{a} + t.$$

The author deduces the formula

$$T = \frac{1 + K}{a} + t,$$

where  $K$  is the variation from the ideal gas,  $\frac{dU_T}{pdv}$ . For hydrogen, the correction  $K/a$  equals  $+0.11^\circ$ . W. D. B.

On the spontaneous evolution of heat from radium salts. *P. Curie and A. Laborde. Comptes rendus, 136, 673 (1903).* — By means of a thermocouple it was shown that a gram of barium chloride containing about one-sixth of its weight of radium chloride was continuously  $1.5^\circ$  hotter than a gram of pure barium chloride kept under apparently similar conditions. The approximate calculation is made that one gram of radium would evolve about 100 cal per hour or one combining weight (225 g) about 22,500 cal per hour, an amount comparable with the heat of combustion of one combining weight of hydrogen burning in oxygen. W. D. B.

Heats of combustion of organic compounds considered as additive properties. *P. Lemoult. Comptes rendus, 136, 895 (1903).* — The author proposes to test for hydrocarbons the accuracy of the formula

$$Q = 157n + A.$$

In this formula  $Q$  is the molecular heat of combustion,  $n$  is the number of carbon atoms in the formula, and  $A$  is a constant which varies for each homologous series. In fifty-three cases out of sixty, the formula agrees with the facts to within less than one percent. W. D. B.

Heats of combustion of organic compounds considered as additive properties. *P. Lemoult. Comptes rendus, 137, 515 (1903).* — It is assumed that the heat of combustion of the primary and secondary alcohols  $C_nH_{2n+1}OH$  can be represented by the equation  $Q = 157n + 10$ . This formula was applied to eight alcohols and stood the test well. Other modifications of the same general formula are used for testing alcohols, for ethers, for aldehydes and ketones. W. D. B.

On the heat of combustion of phosphorus and on the phosphoric anhydrides. *H. Giran. Comptes rendus*, 136, 550 (1903).—The heat of combustion of solid white phosphorus is 369.4 cal. The crystallized phosphoric anhydride evolves the most heat on dissolving in much water, and the vitreous form evolves the least, the amorphous form coming in between the other two. The heat effects confirm the analytical data that phosphorus pentoxide dissolves first as metaphosphoric acid. *W. D. B.*

Heat of neutralization of hydroferrocyanic acid. *P. Chrétien and J. Guinchant. Comptes rendus*, 137, 65 (1903).—The authors have determined the heat of neutralization of hydroferrocyanic acid ( $4 \times 14.47$  cal at  $12^\circ$ ) and the heats evolved when this substance combines with ether or acetone. It was not possible to calculate these last heat effects from the dissociation pressure curves because the presence of water vapor as catalytic agent introduced difficulties. *W. D. B.*

Heats of formation of some nitrogen and sulphur compounds. *M. Delpine. Comptes rendus*, 136, 451 (1903).—Thermochemical data. *W. D. B.*

Heat of formation of some barium compounds. *A. Guntz. Comptes rendus*, 136, 1071 (1903).—Thermochemical data. *W. D. B.*

A new apparatus for preparing gases pure. *H. Moissan. Comptes rendus*, 137, 363 (1903).—The objections to fused calcium chloride, pumice stone soaked in sulphuric acid, etc., are that air is always present, that secondary reactions are liable to take place, and that there is always difficulty with joints and stoppers. The author therefore dries gases by cooling them to  $-50^\circ$ . To purify them he solidifies them and then separates the impurities by fractional distillation. *W. D. B.*

An electrical thermostat. *C. Marié and R. Marquis. Comptes rendus*, 136, 614 (1903).—The bath is heated by a current passing through a platinum wire. A mercury and acetone thermoregulator closes and opens a secondary circuit which regulates the heating by means of a relay. *W. D. B.*

A quartz-glass mercury-arc lamp. *M. Bodenstein. Zeit. Elektrochemie*, 10, 123 (1904).—Heraeus has now placed on the market an Arons lamp made of quartz instead of glass. This can be used as a source of ultra-violet light. *W. D. B.*

#### One-Component Systems

Some physical properties of trimethyl carbinol. *R. de Forcrand. Comptes rendus*, 136, 1034 (1903).—Pure trimethyl carbinol melts at  $25.45^\circ$ . The heat of vaporization gives a value 22.5 for the Trouton constant, from which the author deduces that the liquid is partially polymerized. The author's extension of Trouton's law holds for this substance, the constant being 30.85. *W. D. B.*

On the solidification of fluorine and on the combination of solid fluorine and liquid hydrogen at  $-252.5^\circ$ . *H. Moissan and J. Dewar. Comptes rendus*, 136, 641 (1903).—When the yellow liquid fluorine is cooled to  $-252.5^\circ$ , the boiling-point of hydrogen, it becomes solid and colorless. At this temperature

solid fluorine and liquid hydrogen react instantaneously and with explosive violence. *W. D. B.*

Specific heats and heats of vaporization or of fusion of aniline and some other organic substances. *R. de Forcrand. Comptes rendus, 136, 945 (1903).*—The heats of fusion of aniline, nitrobenzene and benzene are not what they should be according to the author's formula. He consequently assumes that these substances are abnormal, the solid undergoing some change after apparent solidification. No evidence is brought forward, though it would have been perfectly easy to have tested the hypothesis. *W. D. B.*

On a form of the relation  $\phi(p, v, t) = 0$  for liquids. *H. Moulin. Comptes rendus, 136, 881 (1903).*—The author modifies the formula of van der Waals somewhat and writes it

$$p = \frac{a}{\omega^3} - \frac{b_1 \omega^2}{v^{1/2} \omega^2} + \frac{a_1}{v^{1/2} \omega},$$

where  $a = RT$ ,  $\omega^3 = (v - b)/v$ ,  $b_1$  is a constant, and  $a_1 = R'T$ ,  $R'$  being another constant. *W. D. B.*

Remarks on the liquidogenic theories of fluids. *E. Mathias. Comptes rendus, 136, 545 (1903).*—It is suggested that the theoretical difficulties in regard to the critical point disappear if we assume a liquidogenic theory which conforms to the phase rule and to the law of Avogadro. The author assumes that the liquid is made up chiefly of liquidogenic molecules and the vapor chiefly of gasogenic molecules, the liquidogenic molecule being of course the denser. *W. D. B.*

Heat of transformation of white phosphorus into red phosphorus. *H. Giran. Comptes rendus, 136, 677 (1903).*—It is usually stated that 19.2 cal are evolved when white phosphorus changes to red, and this result is attributed to Troost and Hautefeuille. The author says that Troost and Hautefeuille never made any such measurements. From the vapor pressure curves of the two forms, one would calculate a value of approximately 3.7 cal. The author has determined the value experimentally and finds 4.45 cal. *W. D. B.*

On the changes of color of the mercuric iodides at different temperatures. *D. Gernez. Comptes rendus, 136, 889 (1903).*—It is shown that red mercuric iodide becomes orange-yellow at  $-190^\circ$ , while the yellow modification becomes almost white. This was also pointed out some three years earlier by Kastle (5, 529). *W. D. B.*

On the structure of gold-leaf and the absorption spectrum of gold. *J. W. Mallet. Phil. Trans. 202A, 43 (1903).*—Ordinary gold-leaf shows black lines by transmitted light, which are not to be found in gold-leaf precipitated electrolytically. Experiments proved that these lines were due to folds or wires caused by the elastic concentration of the gold-beater's skin immediately after the blow with the hammer.

Some measurements were also made on the ultra-red, the visible, and the ultra-violet spectrum of gold-leaf, of a greenish-blue colloidal gold, of a ruby-red colloidal gold, and of two pieces of glass, one colored red and the other

greenish-blue by gold. Only qualitative data are given, the photographs not being reproduced. *W. D. B.*

**Preparation and properties of a ruthenium silicide.** *H. Moissan and W. Manchot. Comptes rendus, 137, 229 (1903).*—When ruthenium and silicon are fused in an electric furnace, there is formed the compound  $\text{RuSi}$ . This compound has a density of 5.4, is very hard and is attacked by only a few reagents. Fluorine is the only substance which attacks the silicide in the cold. *W. D. B.*

**Reactions of liquid fluorine at  $-187^\circ$ .** *H. Moissan and J. Dewar. Comptes rendus, 136, 785 (1903).*—At  $-187^\circ$  liquid fluorine reacts with violence with sulphur, selenium, phosphorus, arsenic, lime, and anthracene, but does not react with tellurium, antimony, carbon, silicon, boron, or the anhydrides of arsenic, silicon and boron. *W. D. B.*

#### Two-Component Systems

**A study of the dynamic isomerism of thiourea and ammonium thiocyanate.** *J. E. Reynolds and E. A. Werner. Jour. Chem. Soc. 83, 1 (1903).*—Working with a kilogram of material at a time and using an improved method of analysis, it was found that 24.3 percent of ammonium thiocyanate is converted into thiourea when equilibrium is reached at  $170^\circ$ . The complete freezing-point curve for mixtures of thiocyanate and thiourea was also determined, though the stable triple point was not found. The eutectic mixture corresponds very closely to the composition  $\text{CSN}_2\text{H}_4(\text{NH}_4\text{CNS})_3$ , and the authors therefore conclude that this compound is formed. In other respects the theoretical part of the paper is faulty. *W. D. B.*

**The fusibility of mixtures of antimony sulphide and silver sulphide.** *H. Pélabon. Comptes rendus, 136, 1450 (1903).*—The freezing-point curve for antimony sulphide and silver sulphide shows the existence of two maxima, one at  $503^\circ$  for the compound  $\text{Sb}_2\text{S}_3\cdot\text{Ag}_2\text{S}$ , and the second at a temperature not given for the compound  $\text{Sb}_2\text{S}_3\cdot 3\text{Ag}_2\text{S}$ . Owing to an unfortunate misprint, the author speaks of the eutectics as maximum temperatures. The assigning of formulas to the eutectics is not a plan to be commended. *W. D. B.*

**Iodine and sulphur.** *R. Bouloch. Comptes rendus, 136, 1577 (1903).*—From the freezing-point curves for iodine and sulphur it is shown that these substances form no compounds and no solid solutions. The eutectic temperature is  $65.5^\circ$  and the solution contains 54.3 percent sulphur. *W. D. B.*

**Two substances which combine at  $-94^\circ$  and dissociate at  $-79^\circ$ .** *D. Gernez. Comptes rendus, 137, 255 (1903).*—When a solution of mercuric iodide in acetone is cooled below  $-79^\circ$  a solid molecular compound is said to separate, which however liquefies at  $-94^\circ$ . It seems probable that there is some experimental error about this. *W. D. B.*

**Dissociation curves.** *A. Bouzat. Comptes rendus, 136, 1395 (1903).*—“If one arranges in the same group all the univariant systems in which a solid dissociates into another solid and a gas, the ratio of the two temperatures, cor-



responding to the same dissociation pressure for any two systems in the group is constant for all pressures."

"If one arranges in the same group all the univariant systems in which a solid dissociates into another solid and a gas, the change of the entropy, resulting from the setting free of one molecule of gas at a given pressure, is the same for all for the systems of the group." *W. D. B.*

**Sublimation curves.** *A. Bouzat. Comptes rendus, 137, 175 (1903).*—The author has compared the sublimation curves for carbon dioxide, ammonium hydrosulphide, and ammonium carbamate with the curve for  $\text{AgCl} \cdot 3\text{NH}_3$ , and with these substances the law holds:

$$T_A/T_B = \text{const.}$$

In this equation  $T_A$  and  $T_B$  are the absolute temperatures at which the two systems to be compared have any same pressure. *W. D. B.*

**Pressure curves for univariant systems with a gaseous phase.** *A. Bouzat. Comptes rendus, 137, 322 (1903).*—The author considers four types of univariant systems:

- |  |   |
|--|---|
| 1. Solid $\rightleftharpoons$ liquid + vapor | Chlorine hydrate                          |
| 2. Solid $\rightleftharpoons$ solid + vapor  | $\text{NH}_4\text{Cl} \cdot 3\text{NH}_3$ |
| Solid $\rightleftharpoons$ vapor             | Ammonium carbamate                        |
| 3. Liquid $\rightleftharpoons$ vapor         | Acetone                                   |
| 4. Liquid $\rightleftharpoons$ solid + vapor | $\text{NH}_4\text{I} \cdot 3\text{NH}_3$  |

For each group we have the law  $T_A/T_B = \text{const}$ ; but the constant differs from group to group. *W. D. B.*

**Combination of hydroferrocyanic acid with organic compounds.** *P. Chrétien and J. Guinchant. Comptes rendus, 136, 1673 (1903).*—In presence of a trace of moisture, hydroferrocyanic acid will take up an amount of ether which varies with the temperature and may run as high at  $0^\circ$  as 2.7 molecules of ether. Vapor pressure measurements showed that a solid solution is formed. The extraordinary thing is that the ether is not absorbed nor is it evolved when the substances are dry. Acetone, allyl alcohol and other organic substances are absorbed by hydroferrocyanic acid when traces of moisture are present.

*W. D. B.*

**Studies on comparative cryoscopy, I.** *P. W. Robertson. Jour. Chem. Soc. 83, 1425 (1903).*—Fatty acids and their derivatives show increasing polymerization with increasing concentration when dissolved in phenol. While the position and nature of the substituting groups affect the apparent molecular weight, trisubstituted acids are less associated than disubstituted acids, and these latter less than the monosubstituted acids.

*W. D. B.*

**New laws on tonometry which one can deduce from Raoult's experiments.** *E. Wickersheimer. Comptes rendus, 137, 319 (1903).*—The van't Hoff equation for the change of the boiling-point with the concentration is

$$n/N = \frac{\rho d T_1}{2 T_1^2}.$$

The corresponding equation for the freezing-point is

$$n/N = \frac{\lambda d T_2}{2 T_2^2}.$$

Dividing one equation by the other, we have

$$\frac{\rho d T_1}{\lambda d T_2} = \frac{T_1^2}{T_2^2}.$$

W. D. B.

Vapor pressure of aqueous ammonia solution, II. E. P. Perman. *Jour. Chem. Soc.* 83, 1168 (1903). — The vapor composition of aqueous ammonia was determined by the air-current method. The ammonia does not follow Henry's law, but does follow that of van't Hoff and Raoult. The sum of the partial pressures is practically equal to the total pressure as found by the statical method. The author takes this agreement as a proof of the accuracy of the two methods. Those who have worked with the air-current method may draw a different conclusion.

W. D. B.

On the liquefaction of oxygen from the air. G. Claude. *Comptes rendus*, 136, 1659 (1903). — It is well known that nitrogen distils off faster from liquid air than does oxygen, and that an oxygen-rich mixture is left behind. It follows of course that an oxygen-rich liquid will form first when air is cooled to the point of condensation. This has been overlooked or denied by those who take out patents, and the author has consequently tested the matter. The first condensation has the same composition as the last portion of liquid air to evaporate.

W. D. B.

The temperature of calefaction. Bordier. *Comptes rendus*, 136, 459 (1903). — There is a distinct temperature for each liquid under given conditions, at which the liquid does not assume the spheroidal state when falling on a heated metal plate. This temperature is called by the author the temperature of calefaction. For alcohol and water the temperatures lie 50° apart, while the difference between the boiling-points is only 22°. The author has determined the temperatures of calefaction for many strengths of aqueous alcohol, and proposes to use the method as a means of analyzing such mixtures.

W. D. B.

On the sub-salts of barium. A. Guntz. *Comptes rendus*, 136, 749 (1903). — When a barium halide is heated with sodium, there is formed a double salt of the type  $BaXNaX$ . If the double chloride is heated to 700° in *vacuo*, sodium volatilizes, leaving barium chloride behind. When one electrolyzes fused barium chloride,  $BaCl$  is formed at the cathode, which diffuses to the anode and is there oxidized by the chlorine.

W. D. B.

Preparation and properties of the hydride of rubidium and caesium. H. Moissan. *Comptes rendus*, 136, 587 (1903). — At 300° melted rubidium or caesium combines readily with hydrogen, forming a crystallized hydride,  $RbH$  or  $CsH$ . In *vacuo* these compounds dissociate. Water, dry  $SO_2$ , liquid ammonia, and hydrochloric acid gas decompose the hydrides with evolution of hy-

drogen. With fluorine, oxygen, nitrogen, or phosphorus no hydrogen is set free. Carbon, boron and silicon do not react. .  
W. D. B.

The silicides of manganese. *P. Lebeau. Comptes rendus*, 136, 89, 231 (1903). — The author has prepared  $Mn_3Si$  and  $MnSi$  in the electric furnace and describes their properties. When silicon in varying amounts is added to a molten mixture of copper and manganese, the mass when cooled contains  $Mn_3Si$ ,  $MnSi$ , or  $MnSi_2$ , depending on the amount of silicon added. Apparently no copper silicide was formed under the conditions of the experiment.

W. D. B.

The reaction of arsenic on copper. *A. Granger. Comptes rendus*, 136, 1397 (1903). — When copper and arsenic are heated together, there are said to be formed the compounds  $Cu_3As_2$  and  $Cu_5As$ . Both of these lose arsenic on heating. No experiments were made to prove that these substances are really compounds or that they are the only compounds.

W. D. B.

Double carbide of chromium and tungsten. *H. Moissan and A. Kouznetzow. Comptes rendus*, 137, 292 (1903). — Two carbides of chromium,  $Cr_4C$  and  $Cr_5C_2$ , are already known; also two carbides of tungsten,  $Tu_4C$  and  $TuC$ . The authors have now prepared a double carbide of chromium and tungsten,  $Tu_5C_3Cr_5C_2$ .

W. D. B.

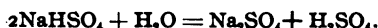
The action of carbon dioxide on potassium hydride. *H. Moissan. Comptes rendus*, 136, 723 (1903). — When dry potassium hydride and dry carbon dioxide are brought together there is no reaction until the temperature reaches  $+54^\circ$ . In presence of traces of moisture the reaction takes place, potassium formate being the product. The minimum amount of water vapor necessary to start the reaction is approximately that which would be in equilibrium with ice at  $-85^\circ$ .

W. D. B.

On the inflammation temperature and on the slow combustion of sulphur in oxygen and in air. *H. Moissan. Comptes rendus*, 137, 547 (1903). — When oxygen (at what temperature?) is bubbled through sulphur, the inflammation temperature is  $282^\circ$ . When air is substituted for oxygen, the inflammation temperature is  $363^\circ$ . Slow combustion without a flame takes place at the lowest temperatures studied. After twelve hours' contact at  $100^\circ$  between sulphur and oxygen, sulphur dioxide could readily be detected on cooling the vapor to  $-186^\circ$ . A similar result was obtained after one month at  $20^\circ$ .

W. D. B.

Displacement by water of the acid in alkali bisulphates. *A. Colson. Comptes rendus*, 136, 366 (1903). — From thermochemical data the author concludes that diluting sodium bisulphate at zero or thereabouts causes the setting free of acid.



The author does not consider the possibility of any other explanation.

W. D. B.

The combination of hydrogen and chlorine under the influence of light. *P. V. Bevan. Phil. Trans.* 202A, 71 (1903). —

(1). The initial expansion is the result of heat developed in the combination of hydrogen and chlorine.

(2). The initial expansion is an effect different from that observed when chlorine is acted on by light. This last effect is due to a rise in temperature, the energy for which is supplied by the light.

(3). The action ceases almost instantaneously when the light is cut off.

(4). The combination is made very much more rapid by the presence of water-vapor.

(5). Small quantities of impurities produce a great decrease in the rate of action.

(6). The induction period may be prolonged indefinitely, but its general character remains the same.

(7). Previous illumination of chlorine, before mixing with hydrogen, makes the action, when light falls on the mixture, faster to begin with—shortens the induction period. This property of isolated chlorine is lost if the chlorine be bubbled through water. Previous illumination of the hydrogen is without effect.

(8). Before any hydrochloric acid is formed, some intermediate body is produced which can act as nucleus, on which a cloud can form on a certain expansion.

(9). The induction period is an essential part of the action, and occurs owing to the formation of intermediate compounds from water-vapor and the two gases. The nature of these compounds is not discovered, but it seems probable that, first, an additive compound of chlorine and water is formed

(perhaps  $\text{H}_2 = \text{O} \begin{array}{c} \text{Cl} \\ || \\ \text{Cl} \end{array}$ , then a hydrogen molecule becomes attached to this,

forming the compound  $\text{H}_2\text{O} \begin{array}{c} \text{Cl} \\ / \quad \backslash \\ \text{O} \quad \text{H}_2 \\ \backslash \quad / \\ \text{Cl} \end{array}$ , and finally this complex body breaks down into  $2\text{H}_2\text{O}$  and  $2\text{HCl}$ .

(10). This view of the process of the combination explains the phenomena of the period of induction and the effect of pre-insolation of the chlorine, and makes it possible to understand the great effect of impurities.

(11). This view of the action of water molecules, in forming additive compounds, can be extended to all those actions where water-vapor, as a catalyzer, seems to be necessary for the progress of the action with finite velocity.

(12). In the case of actions in gaseous systems, conditioned by the presence of a catalyzer, a period of induction must be expected to occur, and the application of the law of mass action to such cases must be made with reference to the intermediate compounds formed. There is, therefore, no reason to expect that agreement will be found between the theory of mass action as applied to the end product equation and the actual experimental results. *W. D. B.*

#### *Multi-Component Systems*

The reduction of metallic halides by hydrogen. *A. Jouniaux. Comptes rendus*, 136, 1003 (1903).—In the reversible equilibrium between a metal, a halide acid, the metallic halide and hydrogen, the square of the acid concen-

tration divided by the hydrogen concentration should be a constant. This means that the ratio of acid to hydrogen at equilibrium should increase with decreasing total pressure. This is found to be the case and the displacement is practically that required by the theory. *W. D. B.*

Action of hydrogen on silver sulphide in presence of the sulphides of antimony and arsenic. *H. Pélabon. Comptes rendus*, 136, 454 (1903). — When hydrogen is allowed to act on a fused mixture of silver and antimony sulphides at a definite temperature, there is more hydrogen sulphide formed the more antimony sulphide is present. Arsenic sulphide acts like the sulphide of antimony. *W. D. B.*

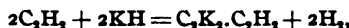
Action of hydrogen on the sulphides of arsenic in presence of antimony and on antimony trisulphide in presence of arsenic. *H. Pélabon. Comptes rendus*, 136, 812 (1903). — "Antimony displaces arsenic completely from its sulphides if the two are liquid. When hydrogen is heated in the presence of antimony sulphide and of a mixture of antimony and arsenic, the proportion of hydrogen sulphide increases with the amount of antimony." *W. D. B.*

Properties of sodium sulphate solutions. *C. Marié and R. Marquis. Comptes rendus*, 136, 684 (1903). — The authors have determined the solubility of sodium chloride in unsaturated solutions of sodium sulphate at temperatures between 14.8° and 34.28°. There is no break in the curve as there certainly would be, were there any temperature at which dissolved sodium sulphate were suddenly dehydrated. *W. D. B.*

Preparation of crystallized zinc and cadmium sulphides. *G. Viard. Comptes rendus*, 136, 892 (1903). — When the vapor of zinc chloride, diluted with carbon dioxide is passed over stannous sulphide, crystallized zinc sulphide can be obtained. By starting with cadmium chloride and carbon dioxide, crystallized cadmium sulphide can be obtained. *W. D. B.*

The etherification of the halide acids. *A. Villiers. Comptes rendus*, 136, 1551 (1903). — Starting with one molecular weight of acid to ten molecular weights of alcohol at 100°, 96.7 percent of hydrochloric acid, 85.5 percent of hydriodic acid and 80.1 percent of hydrobromic acid are converted into the corresponding halide. The reason for the difference in yield appears to be due largely to the formation of ethyl ether, which takes place readily with hydrobromic acid, and to a much lesser extent with hydrochloric acid. *W. D. B.*

Action of acetylene on alkali hydrides. *H. Moissan. Comptes rendus*, 136, 1522 (1903). — When acetylene acts on potassium hydride at 100°, hydrogen is set free. The author writes the reaction



but there is nothing in the data published to show why both sides of the equation should not be divided by two.

Rubidium, caesium, sodium and calcium hydrides react in the same way, though the last two only with difficulty. At 100° ethylene and methane do not react. *W. D. B.*

Effect of a trace of water on the decomposition of alkali hydrides by

acetylene. *H. Moissan. Comptes rendus*, 137, 463 (1903). — When dry acetylene is brought in contact with potassium or sodium hydride, no reaction takes place below  $+42^{\circ}$ . When traces of moisture are present, the reaction takes place vigorously even at  $-60^{\circ}$ .  
W. D. B.

Crystallization of sparingly soluble substances. *A. de Schuilen. Comptes rendus*, 136, 1444 (1903). — By adding dilute sulphuric acid very slowly to a hot solution of barium chloride in aqueous hydrochloric acid, well-formed crystals of barium sulphate can be obtained, which are approximately 0.5 mm in length. Crystallized aluminum hydroxide can be obtained by adding ammonia slowly to an alum solution. A number of minerals have been obtained as crystals in a similar way.  
W. D. B.

The formation of urea by the direct hydrolysis of lead cyanate. *A. C. Cumming. Jour. Chem. Soc.* 83, 1391 (1903). — When lead cyanate is boiled with water, it is converted quantitatively into lead carbonate and urea.  
W. D. B.

Combination of ferric sulphate with sulphuric acid. *A. Recoura. Comptes rendus*, 137, 118, 189 (1903). — When concentrated sulphuric acid in excess is added to a strong solution of ferric sulphate, there is no visible change at first, but after awhile all the iron precipitates as an insoluble white powder, having the composition  $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$ . When this compound is treated with pure water it breaks down at once into ferric sulphate and sulphuric acid, as was shown by freezing-point methods. On heating the acid it loses  $6\text{H}_2\text{O}$  and then dissolves very slowly. The author has prepared the diethyl ester of ferrisulphuric acid.  
W. D. B.

A compound of aluminum sulphate with sulphuric acid. *E. Baud. Comptes rendus*, 137, 492 (1903). — When aluminum sulphate is heated with 75 percent sulphuric acid, there separates, on cooling, the salt  $\text{Al}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ . This is apparently analogous to the chromosulphuric and ferrisulphuric acids.  
W. D. B.

On the expansion of tempered steels. *G. Charpy and L. Grenet. Comptes rendus*, 136, 92 (1903). — No change in the coefficient of expansion occurs when steels containing less than 0.5 percent carbon are quenched from  $700^{\circ}$ – $1000^{\circ}$ . If a steel containing 0.6–1.0 percent carbon be quenched from above  $900^{\circ}$ , there is a sudden contraction when the steel is heated to  $250^{\circ}$ – $350^{\circ}$ . With steels containing more than one percent carbon, quenching from above  $900^{\circ}$  gives rise to two sudden contractions, one when the steel is reheated to about  $150^{\circ}$  and the other at  $300^{\circ}$ . The authors are completely puzzled by this phenomenon.  
W. D. B.

Spontaneous decarburization of steel. *G. Belloc. Comptes rendus*, 136, 500 (1903). — If a steel be heated rapidly in a vacuum to above  $800^{\circ}$ , it loses carbon. If it be heated first to  $550^{\circ}$  to drive out occluded gases, it does not lose carbon when carried above  $800^{\circ}$ .  
W. D. B.

Action of carbon monoxide on iron and its oxides. *G. Charpy. Comptes rendus*, 137, 120 (1903). — When iron is heated in a current of carbon mon-

oxide, there is a precipitation of pulverulent carbon at temperatures between 550° and 750°. Above the latter temperature, the iron takes up carbon, the metal remaining bright. When ferric oxide is heated with carbon monoxide, metallic iron containing more or less carbon is obtained at all temperatures between 200° and 1200°. In a porcelain crucible an iron silicate is formed above 1100°, but the reduction can be accomplished successfully at these temperatures by using a magnesia crucible.

W. D. B.

**On the theory of quenched steels.** *A. Le Chatelier. Comptes rendus, 136, 664 (1903).* — The author believes that there is only one allotropic form of iron, the non-magnetic, and he assumes that the change into the magnetic state takes place at a lower temperature, the more intense the quenching. He maintains that this hypothesis enables him to account for all the known facts in regard to steel, and that it does away with such frivolous assumptions as that of solid solutions. It would not be unreasonable to object that the author succeeds in "accounting for all the known facts" only by being very vague in regard to them.

W. D. B.

**The expansion of nickel steels.** *C. E. Guillaume. Comptes rendus, 136, 303 (1903).* — Data are given for the coefficient of expansion of nickel steels having a nickel content varying from 48.7 to 70.3%. The author has succeeded in making a nickel steel containing 35–36 percent nickel, which has an absolutely negligible coefficient of expansion

$$\alpha = (+0.028 - 0.00232t)10^{-6}.$$

This alloy is now used by the French, Russian, Swedish, and Roumanian governments, and also in Cape Colony.

W. D. B.

**Temporary and permanent changes in nickel steels.** *C. E. Guillaume. Comptes rendus, 136, 356 (1903).* — Bars containing forty-four percent nickel are perfectly suited for the construction of high-grade standards. Bars containing less nickel are fairly permanent, but changes in the length were detected even after six years, so that these bars can only be used as secondary standards.

W. D. B.

**Theory of the nickel steels.** *C. E. Guillaume. Comptes rendus, 136, 1638 (1903).* — It is believed that "the reversible alloys of nickel and steel are composed of reciprocal solutions of nickel and iron, tending to assume a definite equilibrium at each temperature with relative amounts of  $\alpha$  and  $\gamma$  iron." The irreversible alloys would then be those in which the appearance of the  $\alpha$  iron is prevented either by false equilibrium or some other unknown cause.

W. D. B.

**Consequences of the theory of nickel steels.** *C. E. Guillaume. Comptes rendus, 137, 44 (1903).* — It is believed that the nickel steels are the only ones which can have their particular properties because nickel is the only magnetic metal with a transformation temperature lower than that of iron.

W. D. B.

**The microscopic structure of nickel steels.** *L. Guillet. Comptes rendus, 136, 227 (1903).* — With steels containing 0.12 percent carbon and varying amounts of nickel, the structure is practically identical with that of ordinary steels until the amount of nickel reaches ten percent when martensite appears.

With fifteen percent nickel one has practically pure martensite, while white polyhedral crystals appear at higher concentrations, filling the whole field after the nickel content reaches thirty percent. Similar results are obtained with steels containing more carbon, except that a higher nickel content is necessary before the changes take place.

W. D. B.

The effect of certain treatments on the microstructure of nickel steels. *L. Guillet. Comptes rendus*, 136, 502 (1903). — A brief statement of the effect on the microstructure of nickel steels of tempering, annealing, working, chilling, etc. The tempering and working produce very similar results.

W. D. B.

Diagram giving the properties of nickel steels. *L. Guillet. Comptes rendus*, 137, 411 (1903). — The author makes use of a rectangular diagram in which the abscissas are percentages of carbon and the ordinates are percentages of nickel. Four lines are drawn from the point on the  $x$ -axis representing 1.65 percent carbon to points on the  $y$ -axis corresponding to 10, 13, 25, and 29 percent nickel. The field below the 10 percent line contains steels having the same structure as the ordinary carbon steels; the field between the 10 percent and the 13 percent lines represents  $\alpha$ -iron plus martensite; the field between the 13 percent and the 25 percent lines contains pure martensite. Between the 25 percent and the 28 percent lines we have mixtures of martensite with  $\gamma$ -iron, while  $\gamma$ -iron occurs pure above the 28 percent line.

W. D. B.

Properties and constitution of manganese steels. *L. Guillet. Comptes rendus*, 137, 480 (1903). — About half the amount of manganese is needed to produce the same effect as a given amount of nickel. With steels containing more than 0.5 percent carbon, pure martensite is not obtained at all on adding manganese. Instead there is a mixture of martensite and troostite, or even occasionally troostite pure. The pearlite steels containing manganese show a great resistance to shock. The belief that manganese steels are very brittle is due to people having assumed that one could use practically the same concentrations of manganese as of nickel.

W. D. B.

Catalytic decomposition of ethyl alcohol by pulverulent metals. *P. Sabatier and J. B. Senderens. Comptes rendus*, 136, 738, 936 (1903). — Freshly reduced copper acts on alcohol at 200°–250°, forming aldehyde and hydrogen. At 330° traces of ethyl acetal are present. At 420° the aldehyde breaks down partially with formation of methane and carbon monoxide. With nickel the reaction is very slow below 170°, and at 178° the aldehyde begins to break down. Above 230° the carbon monoxide changes to carbon dioxide and carbon. With platinum at 310°, three-quarters of the aldehyde has broken down into methane and carbon monoxide, no carbon and no carbon dioxide being formed.

W. D. B.

Catalytic action of pulverulent metals on alcohols. *P. Sabatier and J. B. Senderens. Comptes rendus*, 136, 921, 983 (1903). — The primary alcohols are decomposed by pulverulent copper into aldehydes and hydrogen; the secondary alcohols into ketones and hydrogen; the tertiary alcohols into water and unsaturated hydrocarbons.

W. D. B.

Catalytic reduction of aldehydes and ketones into alcohols. *F. Sabatier*



and J. B. Senderens. *Comptes rendus*, 137, 301 (1903). — When a mixture of aldehyde vapor and hydrogen is passed over reduced nickel heated to above  $80^{\circ}$ , there is almost quantitative reduction to alcohol, only traces of acetal being formed. At  $115^{\circ}$  a mixture of acetone and hydrogen reduced to propyl alcohol, though the yield is not quantitative. With copper it is therefore possible to decompose the alcohols and with nickel to regenerate them. Copper does not have a catalytic action on aldehyde and hydrogen below  $200^{\circ}$ ; at this temperature the reverse reaction is already a factor and a reversible equilibrium is obtained.

W. D. B.

Catalytic reactions of various metals. A. Trillat. *Comptes rendus*, 137, 187 (1903). — Alcohol and oxygen in presence of platinum or copper give aldehyde. An incandescent platinum wire changes alcohol to aldehyde (plus hydrogen?). In presence of platinum or copper, vapors of methyl alcohol and formaldehyde combine readily to form methylal. On passing the vapors of methylal and water over an incandescent spiral the reverse reaction takes place, methyl alcohol and formaldehyde being regenerated. The copper must be coated with a film of oxide to make it act and it seems to improve with use. [It seems probable that this oxide film is afterwards reduced and that this is merely a way of getting a larger surface of freshly reduced copper.]

W. D. B.

Oxidation of ammonia and the amines by catalytic action. A. Trillat. *Comptes rendus*, 136, 53 (1903). — A hot-cold tube is made with an electrically-heated platinum wire and a glass tube cooled with water. Ammonia is oxidized chiefly to nitrous acid. An aliphatic amine is broken down, the alkyl radical being oxidized to the corresponding aldehyde, while the ammonia is of course also oxidized. Aromatic amines are scarcely affected.

W. D. B.

Oxidation of cobalt and manganese acetates by chlorine. H. Copaux. *Comptes rendus*, 136, 373 (1903). — The pink solution of potassium cobaltous oxalate can easily be oxidized to a green solution of the corresponding cobaltic salt. The pink solution of cobalt acetate becomes greenish on addition of chlorine and a substance can be made to crystallize to which the author ascribes the formula  $[\text{Co}_2(\text{CH}_3\text{CO}_2)_4]_2\text{CoCl}_4\text{OH}_2\text{O}$ . Manganous acetate is oxidized by chlorine to manganic acetate.

W. D. B.

The formula of Caro's acid. M. Mugdan. *Zeit. Elektrochemie*, 9, 980 (1903). — None of the experiments by Armstrong and Lowry, Price or Mugdan enable us to distinguish between  $\text{H}_2\text{SO}_5$  (monobasic) and  $\text{H}_2\text{S}_2\text{O}_6$  (dibasic) as the formula for Caro's acid.

W. D. B.

#### Osmotic Pressure and Diffusion

The cementation of iron. G. Charpy. *Comptes rendus*, 136, 1000 (1903). — It is shown that the diffusion of carbon into iron does not stop when the saturation point is reached, but that it continues until the iron is entirely changed into carbide. This is exactly what one would have expected; but it is very satisfactory to have experimental confirmation.

W. D. B.

#### Velocities

Law of the action of trypsin on gelatine. S. Henri and Larguier des

*Bancels. Comptes rendus*, 136, 1581 (1903). — It is shown that the reaction velocity equation for the action of trypsin on gelatine is the same as that for the action of the diastases on the carbohydrates. *W. D. B.*

**Action of emulsine on salicine and amygdaline.** *V. Henri and S. Lalou. Comptes rendus*, 136, 1693 (1903). — When emulsine acts on a mixture of salicine and amygdaline, the total reaction velocity is greater than either of the single reaction velocities, but less than their sum. This is what one would expect on the assumption that the true catalytic agents are intermediate compounds of the emulsine with the salicine and the amygdaline. *W. D. B.*

**Thermochemical investigations on dye-stuffs.** *J. Schmidlin. Comptes rendus*, 137, 331 (1903). — If one dissolves rosaniline acetate in acetic acid, the heat effect is over at once. If one dissolves rosaniline in acetic acid, there is a heat effect lasting six or seven minutes, the solution becoming more colored all the time. From this the author concludes that rosaniline dissolves as such in acetic acid and that the change to the acetate takes place relatively slowly. Assuming, as a first approximation, that equal heat effects correspond to equal amounts of acetate formed, the author is able to show that the reaction is one of the first order. Thermochemical data are also given for rosaniline and para-rosaniline with hydrochloric, sulphuric, acetic, and oxalic acids. *W. D. B.*

**On the soluble ferments which cause the hydrolysis of the polysaccharides.** *E. Bourquelot. Comptes rendus*, 136, 762 (1903). — It is pointed out that even when one confines oneself to hydrolysis, each special substance needs a special ferment, maltose and maltase, trehalose and trehalase, gentiobiose and gentiobase, touranose and touranase, lactose and lactase, melibiose and melibiase. Since there are numberless organic compounds, the author draws the conclusion that there are also numberless ferments. There would seem to be another possibility, that there may be more names than there are ferments. *W. D. B.*

**The reaction between phosphorus and oxygen, I.** *E. J. Russell. Jour. Chem. Soc.* 83, 1263 (1903). — Phosphorus reacts more rapidly with oxygen dried over sulphuric acid than with oxygen dried over phosphorus pentoxide, but still more water decreases the rate of reaction. Moderately dried oxygen reacts with phosphorus at all pressures, the reaction at higher pressures taking place very slowly, which is probably the reason it has been overlooked hitherto. With moist oxygen no reaction takes place when the oxygen pressure is above 500 mm; but this is due to the formation of a protective film. *W. D. B.*

**Activity of some rare earth salts as oxygen carriers.** *A. Job. Comptes rendus*, 136, 45 (1903). — Both cerous carbonate and lanthanum acetate accelerate the oxidation of hydroquinone. Cerium forms a peroxide and the author deduces the existence of a lanthanum peroxide. *W. D. B.*

#### *Electromotive Forces*

**A law relative to the electromotive force of cells based on the reciprocal action of salt solutions and soluble electrolytes.** *M. Berthelot. Comptes rendus*, 136, 413, 481, 1109, 1497, 1600; 137, 285, 291, 421, 956 (1903). — It is stated that the electromotive force of an acid-alkali cell is the sum of the elec-

tromotive forces due to the action of the acid and the alkali on the neutral salt. There is practically no reference made to the work of others, and the question as to the accuracy of the measurements is not discussed as it should be.

W. D. B.

Effect of temperature on electrocapillary phenomena. A. Gouy. *Comptes rendus*, 136, 653 (1903). — The relative depression of the maximum surface tension of water by different solutes appears to be less the higher the temperature.

W. D. B.

Action of radio-active substances on the electrical conductivity of selenium. E. van Aubel. *Comptes rendus*, 136, 929 (1903). — Hydrogen peroxide decreases the resistance of selenium when placed near it. Turpentine does the same. Consequently the author believes that these two substances must emit some sort of radiation.

W. D. B.

#### *Electrolysis and Electrolytic Dissociation.*

Electrolytic equivalent of silver. H. Pellat and A. Leduc. *Comptes rendus*, 136, 1649 (1903). — The authors have made some experiments on the electrolytic equivalent of silver and reach the conclusion that, under the conditions of their experiments, one coulomb precipitates 1.119–1.120 MgAg. This however is not to the point. Richards has shown that practically all the determinations give the same value when reduced to the same voltameter. It is merely a question which voltameter should be taken as the standard. Richards has explained at length why he considers his voltameter the best. The authors give no reasons why their form should be accepted as the standard.

W. D. B.

The electrolytic formation of per-iodic acid and its salts. E. Müller. *Zeit. Elektrochemie*, 10, 49 (1903). — The advantage of alkaline solutions over neutral or acid solutions in the electrolytic production of per-iodates with platinum anodes is believed to be due to the greater excess voltage. The decreasing yield with rising temperature is attributed to the decreasing excess voltage. The increase of the excess voltage with the length of polarization is cited to explain the fact of the current efficiency increasing with the time.

With lead peroxide anodes a very high yield of per-iodic acid, practically 100 percent, is obtained, but this seems to be due to a chemical oxidation by the lead peroxide. The presence of sulphate or chlorate as ion improves the yield of per-iodic acid when using platinum anodes.

W. D. B.

The electrolytic preparation of trivalent vanadium salts. A. Büllemann. *Zeit. Elektrochemie*, 10, 141 (1904). — Ammonia vanadium alum can be prepared electrolytically with ease, using a two-compartment cell and a clean lead or platinum cathode. The alum occurs both in a blue and a red modification.

W. D. B.

Electrolytic preparation of nitrites from nitrates. W. J. Müller. *Zeit. Elektrochemie*, 9, 978 (1903). — The reduction of nitrate to nitrite was carried on in a two-compartment cell with a porous cup as diaphragm. The anode was platinum, the cathode amalgamated copper, and the current density 1.0–0.5 amp/qdm. The current efficiency is about 85–92 percent until about forty per-

cent of the nitrate has been reduced. The current efficiency then decreases rapidly. The author doubts whether E. Müller (8, 147) has really succeeded in working out technically successful methods of preparing nitrite electrolytically. W. D. B.

The existence of electrolytic peroxides of lead, nickel and bismuth. *A. Hollard. Comptes rendus*, 136, 229 (1903).—When a mixture of lead nitrate and copper nitrate is electrolyzed, the anode deposit corresponds to  $PbO_2$  if the solution is concentrated. With decreasing concentration of lead in the solution, the anode deposit contains more and more oxygen, apparently running even above  $PbO_2$ . With a nickel salt dissolved in alkaline pyrophosphate plus chromic acid (whatever that may actually be), traces of  $NiO_2$  obtained while a lemon-yellow precipitate of  $Bi_2O_3$  was obtained from a bismuth solution. W. D. B.

The electrolytic reduction of potassium chlorate. *D. Tommasi. Comptes rendus*, 136, 1005 (1903).—Attention is called to the fact that in 1877 the author found that potassium chlorate is reduced electrolytically at a zinc anode. No quantitative measurements were made. W. D. B.

On a so-called electrolytic reduction of potassium chlorate. *A. Brochet. Comptes rendus*, 136, 155 (1903).—Reviewed (7, 550) from *Zeit. Elektrochemie*, 9, 160 (1903).

On metal diaphragms. *A. Brochet. Comptes rendus*, 136, 1063 (1903).—Reviewed (8, 73) from *Zeit. Elektrochemie*, 9, 439 (1903).

The electrolysis of the alkali sulphides. *A. Brochet and G. Ranson. Comptes rendus*, 136, 1134, 1195, 1258 (1903).—Reviewed (8, 72) from *Zeit. Elektrochemie*, 9, 509, 531 (1903).

On the electrolytic rectifier. *A. Nodon. Comptes rendus*, 136, 445 (1903).—The electrostatic capacity of the aluminum rectifier reaches the value of one farad per square centimeter of aluminum surface. If we assume a dielectric constant of one, the thickness of the condenser is of the order  $10^{-8}$ . [This conclusion is undoubtedly wrong.] The author believes that no film is formed in phosphate solutions. W. D. B.

The conditions determining the sign and magnitude of electrical endosmose. *J. Perrin. Comptes rendus*, 136, 1388, 1441 (1903).—Attention is called to the relation between the movement of particles in suspension through the water under the influence of electrical stress and the movement of solutions through a rigid porous diaphragm. Experiments are given to show that electrical endosmose is greatest in liquids having a high dielectric constant or having a high dissociating power. [The author makes the mistake of supposing these two statements to be synonymous.]

In aqueous solution, with a barium carbonate diaphragm, many solutions, especially alkaline ones, show a negative endosmose. [Magnesite diaphragms with caustic soda solutions show negative endosmose.] W. D. B.

Electrolytic transference of certain ions in gelatine. *A. Charpentier. Comptes rendus*, 136, 1652 (1903).—With a dilute solution of chromic acid and a gelatine diaphragm there is negative endosmose. W. D. B.

**Dissociation constants of trimethylene carboxylic acids.** *W. A. Bone and C. H. G. Sprankling. Jour. Chem. Soc.* 83, 1378 (1903).—The dissociation constant of trimethylene carboxylic acid is 0.00171; of trimethylene-1:1-dicarboxylic acid is 2.00; of *cis*-trimethylene-1:2-dicarboxylic acid is 2.00; and of *trans*-trimethylene-1:2-dicarboxylic acid is 0.040. Each of these acids has a higher dissociation constant than the corresponding open chain saturated acid from which it may be supposed to have been derived. *W. D. B.*

**On the electrical resistance of metallic hydrides.** *H. Moissan. Comptes rendus*, 136, 591 (1903).—The hydrides of potassium, sodium, rubidium and caesium do not conduct the current to a measurable extent. The hydrides of calcium and of lithium do not conduct even when melted. *W. D. B.*

**Determination of the dissociation of ternary electrolytes by means of isohydric solutions.** *G. Kümmell. Zeit. Elektrochemie*, 9, 975 (1903).—It is not possible to determine the concentration of the ions in a solution of magnesium chloride from conductivity measurements and from the transference number because the concentration and transference number of MgCl are not known. The author determines the concentration of chlorine as ion by finding the concentration of potassium chloride, which is isohydric with the magnesium chloride solution. Since the laws in regard to isohydric solution probably do not hold for these mixtures of binary and ternary electrolytes, the author's results are of questionable accuracy. *W. D. B.*

**On the change of the specific conductivity of salt solutions caused by alkali.** *R. Ehrenfeld. Zeit. Elektrochemie*, 10, 3 (1904).—When caustic soda is added drop by drop to solutions of all sodium salts of organic acids, there is first a decrease and then an increase in the specific conductivity. This is now considered to be due to the forcing back of hydrolysis. The author's previous calculations (7, 552) of the dissociation of certain esters are therefore to be canceled. *W. D. B.*

**Determining the reaction of a liquid by means of indicators.** *H. Friedenthal. Zeit. Elektrochemie*, 10, 113 (1904).—The author has prepared solutions in which the concentration of hydrogen as ion decreases from each to the next by a power of ten and has determined the colors of these solutions when definite quantities of different indicators are added to them. He then uses these as standards in determining the acidity of any unknown solutions. In this way he finds that most of the solutions from different parts of the human body are approximately neutral. *W. D. B.*

#### *Dielectricity and Optics*

**On the discharge of electricity from hot platinum.** *H. A. Wilson. Phil. Trans.* 202A, 243 (1903).—The variation of the negative leak per square centimeter with the temperature can be expressed by Richardson's formula (8, 77), but the total amount of the leak can be reduced by careful cleaning of the wire to 1/250,000 of the value found by Richardson. The discrepancy is probably due chiefly to occluded hydrogen, because hydrogen causes a very large negative leak. *W. D. B.*

**On the photo-electric discharge from metallic surfaces in different gases.**

*W. M. Varley. Phil. Trans. 202A, 439 (1903).* — Experiments were made on the "dependence of the magnitude of the photo-electric current from a metal surface illuminated by ultra-violet light on the pressure and nature of the gas in which the illuminated surface is enclosed." The current in carbon dioxide is greater than that in air and the latter is greater than that in hydrogen. At low pressures, saturation currents are obtained but not at the higher ones. Except for this, the sets of curves obtained can be explained readily by the ionic theory of conduction. *W. D. B.*

**Production of ozone by spirals with high tension and high frequency.**  
*H. Guilleminot. Comptes rendus, 136, 1653 (1903).* — A description of an apparatus which has been very effective in electro-therapy and which should give good results in the preparation of ozone, though the advisability of using copper wires is questionable. *W. D. B.*

**On the magnetic deflection and the nature of certain rays emitted by radium and polonium.** *H. Becquerel. Comptes rendus, 136, 199 (1903).* — By means of a photographic method, the author confirms Rutherford's results (8, 77) on the deflection of the  $\alpha$  rays by means of the magnet. *W. D. B.*

**On the radiation of polonium and radium.** *H. Becquerel. Comptes rendus, 136, 431 (1903).* — The author has succeeded in showing the magnetic deflection of rays from polonium. These behave like the  $\alpha$  rays from radium. *W. D. B.*

**The radiation of polonium and the secondary radiation produced by it.**  
*H. Becquerel. Comptes rendus, 136, 977 (1903).* — The author finds that polonium emits rays which are different from the  $\alpha$  rays and much more penetrating. The secondary radio-activity excited in lead, for instance, appears to be due to these other rays. *W. D. B.*

**On induced radio-activity and the emanations from radium.** *P. Curie. Comptes rendus, 136, 223 (1903).* — The law of the rate of decay of induced radio-activity is found to be the same at  $-180^\circ$  and at  $+450^\circ$  as at ordinary temperatures (7, 142). The author feels that there is not yet sufficient evidence to justify Rutherford's belief that the radium emanations are really a material gas. *W. D. B.*

**On the decay of radio-activity from solids.** *P. Curie and J. Danne. Comptes rendus, 136, 364 (1903).* — For the first two hours and a half, the rate of loss of radio-activity is much greater for solids that have been exposed to radium than for gases. After that the rate is the same. *W. D. B.*

**On the induced radio-activity caused by the salts of actinium.** *A. Debierne. Comptes rendus, 136, 446 (1903).* — Radium causes no radio-activity in a space maintained continually almost at a vacuum, while it causes a uniform activity in a space filled by a gas. Actinium produces an activity in a space filled with gas, but the activity is much more intense close to the actinium than elsewhere. In a space kept almost at a vacuum, actinium produces an activity uniform throughout the space. *W. D. B.*

**Hypothesis on the nature of radio-active substances.** *F. Re. Comptes*

*rendus*, 136, 1393 (1903). — The author assumes that the suns are made of partially-condensed radio-active substances. Further condensation leads to the stable forms which we know as elements. W. D. B.

The absorption spectra of metallic nitrates, II. *W. N. Hartley. Jour. Chem. Soc.* 83, 221 (1903). — "The ultimate conclusion drawn from this work is that the operations of dissolving a salt and diluting the solution do not cause a separation of the compound into ions, but only a dissociation of such a character that the molecule is shown to consist of two parts — the movements of the one being influenced by those of the other, so that the molecule of the salt is, in fact, not completely resolved into ions, but is in a condition of molecular tension. The application of external energy, such as light or electricity, may, however, readily cause a separation, such as may be brought about by electrolysis or by static electricity and, in some instances, by photographic action." W. D. B.

The spectra of neon, krypton and xenon. *E. C. C. Baly. Phil. Trans.* 202A, 183 (1903). — A carefully compiled table of wave-lengths from the spectra of neon, krypton and xenon. The accuracy is believed to be at least  $\pm 0.03$  Ångstrom unit. W. D. B.

#### *Crystallography, Capillarity and Viscosity*

An enquiry into the variation of angles observed in crystals; especially of potassium-alum and ammonium-alum. *H. A. Miers. Phil. Trans.* 202A, 459 (1903). — Experiments were made with growing alum crystals and it was found that "the faces which actually occur upon a crystal are, in general, not those with simple rational indices, but are vicinal faces." Further experiments showed that these "vicinal faces are neither produced nor appreciably affected by the concentration streams in the solution." Contrary to the views of Wulff, the faces actually occurring are "those with complex indices and low reticular density." W. D. B.

The molecular formulæ of fused salts as determined by their molecular surface energy. *J. F. Bottomley. Jour. Chem. Soc.* 83, 1421 (1903). — The rise of fused sodium and potassium nitrates in capillary tubes corresponds to a very high degree of association, approximately nine-fold. W. D. B.

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STUDIES IN VAPOR COMPOSITION, III.  
SATURATION BY THE METHOD OF AIR-BUBBLING

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BY H. R. CARVETH AND R. E. FOWLER

Since the classical researches of Raoult, investigators have sought to determine the molecular weight of substances by measuring the lowering of the vapor pressure of their solutions. To do this two methods are practicable : either to keep the temperature constant and to measure the vapor pressure of solvent and solution, or to keep the pressure constant and to measure the temperatures at which the vapor is in equilibrium with the solvent and the solution. The first of these, the static method, consists in placing a small quantity of the liquid to be investigated in the torricellian vacuum of a barometer and noting the temperature and the fall of the mercury column. Apparently nothing could be more simple. Yet the work of Landolt and later of Kahlbaum has clearly demonstrated that it is next to impossible to free many organic liquids of the two most common impurities, viz., water vapor and air. As the results of this method are not very satisfactory, the second or dynamic method has found more general favor. This consists of the determination of the boiling-point at a fixed pressure. Kahlbaum<sup>1</sup> has tried this method and compared the results with those obtained by the static method. He says: "Die Zahlen haben erwiesen, dass in der That beide Methoden übereinstimmende Resultate ergeben." He states further that there are numerous theoretical reasons why they should agree. The dynamic method has been applied to the determinations of molecular weights of substances in solution; for this work, apparatus has been designed by Beckmann, Landsberger, McCoy, and others. These methods have been tested so frequently that the effect of the most serious errors involved is now known. Such cannot be said of a third method: to find some of its errors and limits of usefulness was the object of the present work.

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<sup>1</sup> Zeit. phys. Chem. 13, 44 (1894).



This method which may be regarded as a dynamic method was based on the principle of saturating a gas with the vapor from a solution or solvent; when there are known the volume, temperature, pressures and the amount of vapor carried over, the partial pressure may be calculated; from these, of course, the molecular weight may be found.

Regnault<sup>1</sup> in 1845 tested this method to see if the results given by it, agreed with those he had obtained by the static method. The liquid chosen was water. Air was passed through a flask containing moistened sponge, through the meshes of wetted silk, then through the absorption tubes into the aspirator where the volume of air passed was measured. Regnault's experiments with the static method had proved to his satisfaction that a substance in a vacuum assumes its maximum tension with great rapidity, but that this is not the case when air is present. A considerable time was then necessary to ensure complete saturation. Another source of error recognized was due to the hygroscopic nature of the glass apparatus which was to be weighed. Working with the greatest care to obtain saturation and constant conditions for weighings, Regnault was able to show that the results obtained agreed within one percent with those calculated from his determinations by the static method. In 1888 Tammann<sup>2</sup> recalculated the results of Regnault; disagreements were then seen to be present ranging from a positive value of 1.59 percent (No. 51) to a negative error of 2.59 percent (No. 60). Of the 68 values thus recalculated, 26 show an excess of water carried over, and 42 a deficiency; it was then evident to Tammann that the use of the method might be extended to determine the vapor tension of other liquids, if certain precautions were taken.

In his experiment a balloon flask fitted with inlet and outlet tube was immersed in a water-bath whose temperature was regulated by an ether thermoregulator. A current of air played on the surface of the water at a distance of 1 cm from it; the moisture-

<sup>1</sup> *Ann. Chim. Phys.* (3) 15, 129 (1845).

<sup>2</sup> *Wied. Ann.* 33, 322 (1888).

laden air was then carried into the sulphuric acid absorption bulbs, which were also immersed in the water-bath. To prevent the carriage of liquid particles an asbestos filter was inserted in the path of the outgoing vapor. It is of interest to note that Tamman found that the time required in the passage of a definite volume of air had no effect on the results — a deduction which must, if care be not taken to define the conditions more exactly, lead to an absolute absurdity. The agreement between calculated values for water and those found by this method agreeing quite well, he then tried to extend the method to salt solutions, bubbling the air through the liquid; for saturated solutions the results were in fair accord with those found by other observers.

In reviewing the work cited above, Ostwald<sup>1</sup> states that he had obtained results which were quite exact by making use of three Liebig bulbs, of which the first held the salt solution, the second pure water, and the third concentrated sulphuric acid. The loss of weight of the second apparatus divided by the increase of weight of the third gave the relative decrease of vapor pressure.

As thus evolved, the method was applied by Walker<sup>2</sup> to the determination of the molecular weights of substances in dilute aqueous solution. Since the variations of temperature did not affect the ratio of the vapor pressures to any great extent, it was not necessary that the control of the temperature should be close, so long as solution and solvent were at the same temperature. Walker was thus able to make use of an air thermostat; the precautions he suggested were to have the bulbs not too full, and the horizontal tubes clean and dry; asbestos filters or plugs were of no great advantage. The results obtained with the aqueous solutions were fairly satisfactory.

The work of Walker was soon followed by that of Will and Bredig,<sup>3</sup> who improved the apparatus and extended the method to alcoholic and ethereal solutions. Since that time,

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<sup>1</sup> *Zeit. phys. Chem.* 2, 436 (1888).

<sup>2</sup> *Ibid.* 2, 602 (1888).

<sup>3</sup> *Ber. chem. Ges. Berlin*, 22, 1084 (1889).

Orndorff and Carrell,<sup>1</sup> and more recently Speyers<sup>2</sup>, have attempted to apply the method with varying results. Since by this method it should be possible to determine the molecular weight of unknown substances with the most common of laboratory appliances, it certainly seems strange that it has not found favor with organic chemists, and placed by them on the same footing as the determination of vapor density by the Victor Meyer method. It might be suitable for those substances which readily decompose on heating and would certainly seem to possess an advantage over any method which involves the use of the delicate and costly Beckmann thermometer. One possible reason for this is that some may have tried the method but have failed to publish their results, owing to their unsatisfactory nature; it is certain that the writers of two papers cited above regarded their papers as merely preliminary in character, but as no work on the subject from their pens has since appeared, it is possible that they also have had considerable difficulty with the method.

The saturation of air by water-vapor has been given a very complete test by Shaw,<sup>3</sup> whose work appears to have been overlooked by almost every writer on this subject. The methods of Regnault, which he employed for complete saturation of the air, for absorption and for weighing, were all examined with considerable care, and a number of sources of error indicated. After the experimental work in this paper had been finished, there appeared a paper by Perman,<sup>4</sup> in which the most important conclusion insofar as the present subject is concerned is that "when air is aspirated through water it becomes saturated with aqueous vapor with great rapidity." The experiments from which this conclusion was drawn are not given in detail.

Some years ago we attempted to use the air-bubbling method to obtain the molecular weight of silver nitrate when dissolved in anhydrous pyridine and obtained the surprising result that its molecular weight was 17, or only one-tenth of its value found in

<sup>1</sup> Jour. Phys. Chem. 1, 253 (1897).

<sup>2</sup> Ibid. 1, 766 (1897); Am. Jour. Sci. (4) 13, 213 (1902).

<sup>3</sup> Shaw. Phil. Trans. A179, 73 (1888).

<sup>4</sup> Perman. Proc. Roy. Soc. 72, 72 (1903).

other ways. Since the work was conducted with considerable care (the Walker method being followed in every detail), it seemed that the result must have been due to errors in the method, rather than to errors of operation and calculation. As the molecular weight of the solute is inversely proportional to the difference in the vapor pressure of solvent and solution, it follows that the observed vapor pressure of the solution was much too small to conform to theory. To account for this, it is necessary to assume that there must have been disturbing factors of unknown value in the experimental operation of this method, such as might be due to viscosity or to surface tension. It will readily be seen that the early investigators, one and all, contented themselves with proving that if dry air bubbled with sufficient slowness through a liquid contained in from one to three Liebig or Geissler bulbs, that it would become *nearly* saturated with the vapor of that liquid.

To judge as to the velocity with which a gas becomes saturated with a liquid, we may refer for a moment to other analogous cases which have been examined more carefully. Very few chemists realize how difficult it is in many cases to form a saturated aqueous solution by shaking a salt or a liquid with a solvent at a constant temperature — in some cases weeks pass before equilibrium is reached. As the solution changes from zero concentration to saturation, the actual amount dissolved in a unit of time becomes smaller and smaller. If, working in the opposite direction, one starts with a more concentrated solution formed at a different temperature (usually higher) and changes it to the desired temperature, there is formed a supersaturated solution which, by the addition of the precipitating phase, passes to a saturated solution. It can most probably be assumed that conditions prevail in the formation of saturated gaseous solutions similar to those present in liquid solutions.

The questions at once arise: Is the same result obtained when treating a gas with water vapor to saturation, as when bringing the gas from a condition of supersaturation to saturation, and have all results obtained hitherto been obtained from gases not completely saturated?

In order to answer these questions a method had to be devised which in its simplest form was carried out in the following manner: Dry air was passed successively through a weighed bulb containing the liquid to be investigated; through a bulb of the same liquid at a somewhat higher temperature; through a condensing tube at the same temperature as the first bulb in order to remove the condensed vapor, and finally through a bulb in which the vapor was completely absorbed. In this manner the dry air was first saturated with vapor by passing through the liquid, the amount dissolved being equal to the loss in weight of the first bulb. The same current of air was then brought into contact with the liquid phase at a higher temperature, then back to its original temperature in a way such that the supersaturation should be overcome. From this supersaturation bulb the air passed through absorption bulbs whose increase in weight was then equal to the vapor which had been held in solution by the air.

The liquid tested was pure water; the operations were carried out in the following manner. Two Liebig bulbs containing distilled water were connected and immersed in a water thermostat at room temperature (about  $20^{\circ}$ ) which was constantly stirred by means of a water motor. The purpose of the second bulb was to serve as a check on the first. From the second bulb a short tube made connections with a third Liebig bulb which contained distilled water and was immersed in a water thermostat kept from  $10^{\circ}$ – $15^{\circ}$  above the room temperature. From this third bulb a glass tube led to the condenser bulb, which consisted of a U-tube filled with glass beads; these were moistened with distilled water. Following this was a weighed Liebig bulb containing distilled water to serve as a check on the efficiency of the condenser. In order to maintain the condenser and its check bulb at the same temperature as the first two bulbs, all four bulbs were immersed in the same bath. From the last bulb a glass tube led to a bulb containing concentrated sulphuric acid; this was placed outside of the first thermostat. This was likewise followed by a check bulb containing sulphuric acid. Air dried by one soda lime and two sulphuric

acid towers was forced through this system by means of an aspirator consisting of two carboys, one being placed a meter above the other, the water being siphoned from the upper to the lower. The air was forced through the system very slowly so as to produce the ideal conditions for saturation in the first bulb. In order that the difference in the loss in weight of the first bulb and the gain in weight of the sulphuric acid should greatly exceed the extent of experimental error, it became necessary to run the apparatus until at least two or three grams of water had been carried over. It was found after a few trials that the length of time required to evaporate this amount of water was too great to give reliable data as the bulbs were soon befouled by the water bath. To obviate this, both thermostats were run at a higher temperature, about  $50^{\circ}$  for the first and  $60^{\circ}$  for the second. After this had been tried a few times, it was noticed that condensation occurred in the connecting tubes which were just above the surface of the water in the thermostats. Hence the connections, as far as possible, were likewise immersed with the result that the rubber connections became softened by the hot water of the thermostats, thus producing extensive leakages. Hence the results of a very considerable number of trials with water thermostats had to be discarded, the observer being thoroughly convinced that he at least was unable to make constant and reproducible weighings (to milligrams) when rubber connections and glass bulbs were used in the water thermostats, especially in experiments requiring from twenty-four to forty-eight hours.

To avoid this difficulty, we decided to use an air-bath thermostat. This consisted of two concentric cylinders of sheet copper, joined like the thermostat of D'Arsonval, except that the air space in which was placed the weighed apparatus was kept at the desired temperature by the vapor of boiling alcohol in the annular space surrounding it. Two such thermostats were constructed of the same size, each having a reflux condenser attached and a close-fitting and well protected cover, the latter having an asbestos gasket, which practically prevented external currents of air from entering the inner cylinder and altering its temperature. Each thermostat had also a short copper tube, 2

cm in diameter, extending just through the annular space, thus making a connection between the interior and the outside, immediately below the lid. When the two thermostats were placed so that these openings were very close together, a large cylindrical cork could enter each opening nearly one-half the length of the cork. Through the latter, two holes permitted the passage of glass tubes connecting the bulb at the higher temperature with the rest of the apparatus. In this arrangement, the system of bulbs and tubes was completely surrounded by warm air at constant temperature, and the very short connections between the two thermostats were well jacketed with the cork. For the study of the vapor pressure of water, methyl alcohol was used as the boiling liquid in one thermostat and ethyl alcohol in the thermostat the higher temperature. This gave for the temperatures of the air-baths about  $63^{\circ}$  and  $75^{\circ}$  respectively.

As the available space in the thermostats was not very great, U-tubes were substituted for Liebig bulbs as far as possible. Three U-tubes were constructed as described by Benedict;<sup>1</sup> these are virtually the same as a Schmitz tube, except that they are entirely of glass (to avoid the possibility of leaky rubber stoppers). For a similar reason the rubber connections were replaced by continuous glass tubes wherever practicable. Thus constructed, the apparatus gave complete satisfaction insofar as connection, weighing, etc., are concerned; the difficulties which later occurred are attributable to other causes. The bulb condenser for this apparatus consisted of a U-tube filled with garnets. It was found, however, after a time, to be nearly impossible to free the garnets entirely from soluble matter, so resort was had to glass wool in place of the garnets. This proved, after all, to be a very poor substitute, and it became necessary to return to the use of glass beads which could be easily and thoroughly cleaned. A non-attackable metal, such as platinum, would be more suitable for the purpose. In fact it would probably be advantageous to have the complete apparatus made of metal.

The component parts of the system may now be mentioned

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<sup>1</sup> *Am. Chem. Jour.* 23, 326 (1900).

in the order of passage of the air current: (1) a long glass coil for warming the dry air current to the temperature of the thermostat ( $63^{\circ}$ ) (the necessity of this had been indicated by experiments of Regnault); (2), (3), and (4) U-tubes of the Benedict form with glass wool in one arm, containing distilled water; (5) a Liebig bulb with water ( $75^{\circ}$ ); (6) an empty U-tube ( $63^{\circ}$ ); (7) a large U-tube containing glass wool moistened with water ( $63^{\circ}$ ); (8) a small U-tube with moist glass wool ( $63^{\circ}$ ); (9) and (10) two U-tubes (Benedict form) with concentrated sulphuric acid ( $63^{\circ}$ ); a tube then led to a second sulphuric acid bulb outside the apparatus. In its operation it was found no easy task when starting and stopping the air current to prevent the sucking back of the liquids which, since everything was enclosed, could be determined only by the final weighings of the bulbs. In order to prevent this sucking back, the air in place of being forced was drawn through the system.

After several trials, especially those of long duration, the capacity of the first tube containing sulphuric acid was found to be too small, so it was replaced by a small Liebig bulb filled with concentrated acid.

The two following series of results were obtained; the first column gives the bulb number, content and temperature, the second column the original weight of the bulb, the third the final weight, and the fourth the difference in weight. Table I shows the results obtained when the U-tubes were filled with glass wool and provided with rubber stoppers and connections.

TABLE I.

I.	II.	III.	IV.
	Original weight	Final weight	Difference in weight
(2) Water $62^{\circ}$	28.1458	24.9742	-3.1716
(3) Water $62^{\circ}$	25.6917	24.9954	-0.6963
(4) Water $62^{\circ}$	17.7470	17.7742	+0.0272
(9) Sulphuric $62^{\circ}$	29.2247	32.3541	+3.1293
(10) Sulphuric $62^{\circ}$	74.7226	74.7557	+0.0331



The total loss of weight was 3.8907 grams, while from the supersaturated solution after it was cooled down to 62°, there was obtained only 3.1624 grams of water. This points to an error of considerable importance. This is probably due to the fact that the rubber stoppers had been very slightly moistened with glycerine. In the next series of results (Table II) glass stoppers or sealed tops were used, the other conditions remaining exactly the same.

TABLE II.

I.	II.	III.	IV.
(2) Water 63°	27.9466	25.5148	-2.4312
(3) Water 63°	26.7427	26.7478	+0.0051
(4) Water 63°	17.1206	17.1030	-0.0176
(9) Sulphuric 63°	28.5960	31.2945	+2.6985
(10) Sulphuric 63°	80.2636	80.3146	+0.0510

By the passage of 15 liters of air ( $t = 23^\circ$ ,  $p = 740$ ) in  $38\frac{1}{2}$  hours, it was found that while by the method of saturating there was lost 2.4261 grams, the air passing from the supersaturated solution gave up 2.7495 grams of water. One source of error has thus been eliminated. It is to be observed that the rate of bubble passage had been so controlled that the change of weight of the second water bulb was very slight, as compared with the previous experiment. The sulphuric acid still fails to effect complete condensation.

The results might possibly be explained on the assumption that there was formed in the first bulbs solutions of silicate in water, resulting from the presence of the glass wool. These bulbs were therefore replaced by U-tubes containing glass beads, the first tube being supplied, like the Benedict, with a side-arm. These U-tubes were all supplied with one-hole rubber stoppers, through which passed connecting tubes.

The arrangement of the apparatus is more readily conducted and manipulated than the former, while the results obtained show that some errors have been eliminated. Fifteen and four-tenths liters of air ( $t = 21.5$ ,  $p = 744.18$ ) were drawn

rather rapidly through the apparatus—time, 21 hours. The temperature of the thermostats was 62° and 73°.

TABLE III.

I.	II.	III.	IV.
(2) Water 62°	39.3796	36.4251	-2.9545
(3) Water 62°	39.7492	39.7725	+0.0253
(4) Water 62°	36.2168	36.0339	-0.1729
(9) Sulphuric	46.8938	50.1091	+3.2153
(10) Sulphuric	42.3151	42.3185	+0.0034

While therefore the bulbs lost 2.9292 grams, there was taken up by the sulphuric acid 3.2187 grams or nearly 9 per cent more water. It is apparent that the method is not yet completely satisfactory, since the check bulb (3) in place of losing a small amount, actually increases in weight, while the check bulb (4), which should have remained almost constant, shows in this last experiment a decrease in weight which affects results very seriously. So far as could be decided from the temperature indicated by the thermometers in the air thermostat, the results may not be explained by temperature differences there.

Of the experiments planned, only the preliminary ones have been performed, the work being published owing to withdrawal from this laboratory of one of the writers; the subject may be taken up again at a later date. Sufficient results have been obtained in the comparative study of the saturation and super-saturation of air by water at a temperature of 62° to suggest that the ordinary method of bubbling air through a solvent or solution to produce complete saturation of the air may be very inaccurate in practice; that only under very especial precautions indeed can such absolute saturation be obtained. Certainly, after examining the very careful work of Regnault and of Shaw and noting the conclusion of the latter<sup>1</sup> "that for saturated air the result of the chemical method is slightly less than the tabulated saturation pressure" one must conclude that to ob-

<sup>1</sup> loc. cit. p. 96.

tain consistent results with a low percentage error requires the greatest of care even when the gas is being passed through a liquid not subject to concentration changes. The difficulties are of course increased when solutions are being treated ; but for these cases the sources of error have not as yet been carefully examined. The results of the paper show, moreover, that it is easy to obtain conditions of supersaturation which are not readily displaced to equilibrium by the presence of an excess of the solute phase. Differential methods involving incomplete saturation may be employed, but under such conditions, proof must be adduced as to the applicability of each particular case. The frequent failures in the application of the air-bubbling method require that the whole method be carefully examined before new results obtained by its use are accepted.

*Cornell University.*

# ON THE STABILITY OF THE EQUILIBRIUM OF A HOMOGENEOUS PHASE

BY PAUL SAUREL

In his memoir *On the Equilibrium of Heterogeneous Substances*, Gibbs has given the conditions which must be satisfied by a homogeneous phase in equilibrium in order that this equilibrium be stable. As the section of Gibbs's memoir in which these conditions are established<sup>1</sup> does not seem to be as well known as some of the other portions of that work, the following discussion of the criteria of stability may be of interest. The attentive reader will not fail to note that our demonstrations, though different in form, are, in substance, the same as those of Gibbs.

The fundamental assumption concerning a homogeneous phase in equilibrium is that its energy  $\epsilon$  is a continuous one-valued function of its entropy  $\eta$ , its volume  $v$ , and the masses  $m_1, m_2, \dots, m_n$  of its independent components. In symbols

$$\epsilon = f(\eta, v, m_1, m_2, \dots, m_n). \quad (1)$$

This assumption is one of the many forms of the so-called principle of continuity.

From equation 1 it follows that if we consider two adjacent states of equilibrium of the homogeneous phase, the change in energy  $\Delta\epsilon$  that accompanies the transformation from one of these states to the other is given by the equation

$$\begin{aligned} \Delta\epsilon = & \frac{\partial f}{\partial \eta} \Delta\eta + \frac{\partial f}{\partial v} \Delta v + \sum_{i=1}^n \frac{\partial f}{\partial m_i} \Delta m_i \\ & + \frac{1}{2} \left\{ \frac{\partial^2 f}{\partial \eta^2} \Delta\eta^2 + 2 \frac{\partial^2 f}{\partial \eta \partial v} \Delta\eta \Delta v + \frac{\partial^2 f}{\partial v^2} \Delta v^2 \right. \\ & + 2 \sum_{i=1}^n \frac{\partial^2 f}{\partial \eta \partial m_i} \Delta\eta \Delta m_i + 2 \sum_{i=1}^n \frac{\partial^2 f}{\partial v \partial m_i} \Delta v \Delta m_i \\ & \left. + \sum_{i=1}^n \sum_{j=1}^n \frac{\partial^2 f}{\partial m_i \partial m_j} \Delta m_i \Delta m_j \right\} + \dots \end{aligned} \quad (2)$$

<sup>1</sup> Trans. Conn. Acad. 3, 156-172 (1876).

in which  $\Delta\eta$ ,  $\Delta v$  and the  $\Delta m$ 's are the changes in the entropy, the volume and the masses of the independent components. The omitted terms are of the third and higher orders.

To obtain the various forms of the criterion of stability, it is sufficient to make the following assumption: In order that the equilibrium of the homogeneous phase be stable, it is necessary and sufficient that the expression in brackets in equation 2 be positive for all values of  $\Delta\eta$ ,  $\Delta v$  and the  $\Delta m$ 's. In other words, the expression in question must be a positive quadratic form. If we represent the quadratic function by  $P$ , the condition of stability is given by the inequality

$$P > 0. \quad (3)$$

Instead of saying that  $P$  is a positive quadratic form, Gibbs makes the equivalent statement<sup>1</sup> that the stability of the homogeneous phase depends upon the same conditions in regard to the second differential coefficients of the energy regarded as a function of the entropy, the volume and the masses of the several components, which would make the energy a minimum, if the necessary conditions in regard to the first differential coefficients were fulfilled.

The condition of stability can be expressed in a variety of other forms which we shall now develop.

In the first place, the temperature  $t$  of the phase in equilibrium, its pressure  $p$  and the chemical potentials  $\mu_i$  of its components are given by the equations

$$t = \frac{\partial f}{\partial \eta}, \quad -p = \frac{\partial f}{\partial v}, \quad \mu_i = \frac{\partial f}{\partial m_i}. \quad (4)$$

These equations enable us to write equation 2 in the form

$$\Delta\epsilon - t\Delta\eta + p\Delta v - \sum_{i=1}^n \mu_i \Delta m_i = \frac{1}{2}P. \quad (5)$$

From this equation and the fundamental inequality 3 it follows that the condition of stability can be written in the form<sup>2</sup>

<sup>1</sup> l. c. p. 163.

<sup>2</sup> l. c. p. 163.

$$\Delta\epsilon - t\Delta\eta + p\Delta v - \sum_{i=1}^n \mu_i \Delta m_i > 0. \quad (6)$$

Again, it follows without difficulty from equations 4 that

$$\Delta t \Delta \eta - \Delta p \Delta v + \sum_{i=1}^n \Delta \mu_i \Delta m_i = P. \quad (7)$$

To show this we observe that equations 4 yield at once the equations

$$\begin{aligned} \Delta t &= \frac{\partial^2 f}{\partial \eta^2} \Delta \eta + \frac{\partial^2 f}{\partial \eta \partial v} \Delta v + \sum_{i=1}^n \frac{\partial^2 f}{\partial \eta \partial m_i} \Delta m_i + \dots \\ -\Delta p &= \frac{\partial^2 f}{\partial v \partial \eta} \Delta \eta + \frac{\partial^2 f}{\partial v^2} \Delta v + \sum_{i=1}^n \frac{\partial^2 f}{\partial v \partial m_i} \Delta m_i + \dots \\ \Delta \mu_i &= \frac{\partial^2 f}{\partial \eta} \Delta \eta + \frac{\partial^2 f}{\partial m_i \partial v} \Delta v + \sum_{j=1}^n \frac{\partial^2 f}{\partial m_i \partial m_j} \Delta m_j + \dots \end{aligned} \quad (8)$$

in which the omitted terms are of the second and higher orders. If we multiply these equations by  $\Delta \eta$ ,  $\Delta v$ ,  $\Delta m_i$  and add, we see that, if we neglect terms of the third and higher orders, equation 7 will hold. From this equation and inequality 3 we obtain at once the following form for the criterion of stability:<sup>1</sup>

$$\Delta t \Delta \eta - \Delta p \Delta v + \sum_{i=1}^n \Delta \mu_i \Delta m_i > 0. \quad (9)$$

This condition yields at once the following familiar theorems:

If a homogeneous phase of constant mass, in stable equilibrium, be heated or cooled under constant pressure or under constant volume, the changes in temperature and in entropy have the same sign.

If a homogeneous phase of constant mass, in stable equilibrium, be compressed or expanded isothermally or adiabatically, the changes in pressure and in volume have opposite signs.

Another interesting result is obtained by supposing that all

<sup>1</sup> l. c. p. 168.

of the masses but one remain unchanged, and that the temperature or the entropy and the pressure or the volume also remain unchanged. The inequality then reduces to the form

$$\Delta\mu_i\Delta m_i > 0. \quad (10)$$

Thus, at constant temperature or entropy and under constant pressure or volume, an increase in the mass of one of the components increases the chemical potential of that component. This result can be stated in a more striking form if we adopt the suggestion of Perrin<sup>1</sup> and define the chemical affinity of the phase for one of its components as the negative of the chemical potential of that component. We may then say that the affinity of the phase for one of its components is diminished by the addition of that component to the phase.

Although the form of the function which appears in equation 1 is unknown, it is nevertheless easy to show that it must be homogeneous and of the first degree. We may therefore write

$$\epsilon = \eta \frac{\partial f}{\partial \eta} + v \frac{\partial f}{\partial v} + \sum_{i=1}^n m_i \frac{\partial f}{\partial m_i}, \quad (11)$$

or, in virtue of equations 4,

$$\epsilon = t\eta - pv + \sum_{i=1}^n \mu_i m_i. \quad (12)$$

From this equation it follows that

$$\begin{aligned} \Delta\epsilon &= t\Delta\eta - p\Delta v + \sum_{i=1}^n \mu_i \Delta m_i \\ &+ \eta\Delta t - v\Delta p + \sum_{i=1}^n m_i \Delta\mu_i \\ &+ \Delta t\Delta\eta - \Delta p\Delta v + \sum_{i=1}^n \Delta\mu_i \Delta m_i. \end{aligned} \quad (13)$$

Equations 5 and 7 enable us to write this in the form

<sup>1</sup> *Traité de Chimie Physique*, 1, 244 (1903).

$$\eta\Delta t - v\Delta p + \sum_{i=1}^n m_i \Delta \mu_i = -\frac{1}{2}P, \quad (14)$$

and this yields a new form for the criterion of stability:<sup>1</sup>

$$\eta\Delta t - v\Delta p + \sum_{i=1}^n m_i \Delta \mu_i < 0. \quad (15)$$

The introduction of the free energy  $\psi$ , the heat function  $\chi$  and the thermodynamic potential  $\zeta$  defined by the equations

$$\psi = \epsilon - t\eta, \quad (16)$$

$$\chi = \epsilon + pv, \quad (17)$$

$$\zeta = \epsilon - t\eta + pv, \quad (18)$$

will enable us to express the condition of stability in three other ways.

From equation 16 we get

$$\Delta\epsilon = \Delta\psi + t\Delta\eta + \eta\Delta t + \Delta t\Delta\eta. \quad (19)$$

In virtue of this relation equation 5 becomes

$$\Delta\psi + \eta\Delta t + p\Delta v - \sum_{i=1}^n \mu_i \Delta m_i + \Delta t\Delta\eta = \frac{1}{2}P, \quad (20)$$

so that the condition of stability takes the form

$$\Delta\psi + \eta\Delta t + p\Delta v - \sum_{i=1}^n \mu_i \Delta m_i + \Delta t\Delta\eta > 0. \quad (21)$$

Two special cases of equation 20 are of interest. If  $t$  remains constant, equation 20 becomes

$$[\Delta\psi + p\Delta v - \sum_{i=1}^n \mu_i \Delta m_i]_t = \frac{1}{2}[P]_t, \quad (22)$$

in which the subscript indicates that  $t$  is supposed to remain constant. We thus find<sup>2</sup> that if the equilibrium is stable

<sup>1</sup> Trans. Conn. Acad. 3, 164 (1876).

<sup>2</sup> l. c. p. 165.



$$[\Delta\psi + p\Delta v - \sum_{i=1}^n \mu_i \Delta m_i]_t > 0. \quad (23)$$

If, on the other hand,  $v$  and the  $m$ 's remain constant, equation 20 becomes

$$[\Delta\psi + \eta\Delta t]_{v,m} + [\Delta t\Delta\eta]_{v,m} = \frac{1}{2}[P]_{v,m}. \quad (24)$$

From equation 7, however, we have

$$[\Delta t\Delta\eta]_{v,m} = [P]_{v,m}; \quad (25)$$

equation 24 therefore becomes

$$[\Delta\psi + \eta\Delta t]_{v,m} = -\frac{1}{2}[P]_{v,m}. \quad (26)$$

From this it follows at once<sup>1</sup> that if the equilibrium is stable

$$[\Delta\psi + \eta\Delta t]_{v,m} < 0. \quad (27)$$

Having thus shown that, if the equilibrium is stable, inequalities 23 and 27 hold, we shall now show that, conversely, if inequalities 23 and 27 hold, then the equilibrium will be stable. To show this it will be sufficient to show that equation 20 is a consequence of equations 22 and 24; for it then follows at once that, if 23 and 27 are satisfied, so also will be the condition of stability 9.

To show that equation 20 is a consequence of equations 22 and 24, let us cause the homogeneous phase to pass from one state of stable equilibrium to an adjacent state of stable equilibrium and let us suppose that the change in question consists of two partial changes, during the first of which  $t$  remains constant, while during the second  $v$  and the  $m$ 's remain constant. For the first change equation 22 will hold, while for the second change we may write the equation which is obtained from 24 by replacing  $\psi$  and  $\eta$  by  $\psi + [\Delta\psi]_t$  and  $\eta + [\Delta\eta]_t$ . If we add these equations and omit terms of the third and higher orders we find that for the total change the following equation holds:

$$\begin{aligned} \Delta\psi + \eta\Delta t + p\Delta v - \sum_{i=1}^n \mu_i \Delta m_i + \Delta t[\Delta\eta]_t + \Delta t[\Delta\eta]_{v,m} \\ = \frac{1}{2}[P]_t + \frac{1}{2}[P]_{v,m}. \end{aligned} \quad (28)$$

<sup>1</sup> l. c. p. 165.

But

$$[\Delta\eta]_t + [\Delta\eta]_{v,m} = \Delta\eta,$$

and

$$[P]_t + [P]_{v,m} = P,$$

if we neglect terms of the third and higher orders. Equation 28 thus transforms at once into equation 20. Equation 20 is thus a consequence of equations 22 and 24; it follows that whenever conditions 23 and 27 are satisfied so also is the condition of stability 9.<sup>1</sup>

The consideration of the function  $\chi$  yields analogous conditions. From equation 17 we get

$$\Delta\epsilon = \Delta\chi - p\Delta v - v\Delta p - \Delta p\Delta v, \quad (29)$$

and this, taken in connection with equation 5, gives

$$\Delta\chi - v\Delta p - t\Delta\eta - \sum_{i=1}^n \mu_i \Delta m_i - \Delta p\Delta v = \frac{1}{2}P. \quad (30)$$

We thus get the following condition analogous to condition 21

$$\Delta\chi - v\Delta p - t\Delta\eta - \sum_{i=1}^n \mu_i \Delta m_i - \Delta p\Delta v > 0. \quad (31)$$

From equation 30 we get the two special results:

$$[\Delta\chi - t\Delta\eta - \sum_{i=1}^n \mu_i \Delta m_i]_p = \frac{1}{2}[P]_p, \quad (32)$$

and

$$[\Delta\chi - v\Delta p]_{\eta,m} - [\Delta p\Delta v]_{\eta,m} = \frac{1}{2}[P]_{\eta,m}. \quad (33)$$

Equation 32 yields the inequality

$$[\Delta\chi - t\Delta\eta - \sum_{i=1}^n \mu_i \Delta m_i]_p > 0, \quad (34)$$

and, if we observe that

$$-[\Delta p\Delta v]_{\eta,m} = [P]_{\eta,m}, \quad (35)$$

equation 33 yields the inequality

<sup>1</sup> l. c. p. 165.

$$[\Delta\chi - v\Delta p]_{\eta, m} < 0. \quad (36)$$

By a demonstration in all respects similar to the one by which we showed that conditions 23 and 27 are equivalent to the condition of stability 9, it can be shown that conditions 34 and 36 are also equivalent to that condition of stability.

Finally, from equation 18 we get

$$\Delta\epsilon = \Delta\zeta + t\Delta\eta + \eta\Delta t - p\Delta v - v\Delta p + \Delta t\Delta\eta - \Delta p\Delta v, \quad (37)$$

and this, with equation 5, gives

$$\Delta\zeta + \eta\Delta t - v\Delta p - \sum_{i=1}^n \mu_i \Delta m_i + \Delta t\Delta\eta - \Delta p\Delta v = \frac{1}{2}P. \quad (38)$$

We thus get the condition of stability in the form

$$\Delta\zeta + \eta\Delta t - v\Delta p - \sum_{i=1}^n \mu_i \Delta m_i + \Delta t\Delta\eta - \Delta p\Delta v > 0. \quad (39)$$

From equation 38 we also derive the equations

$$[\Delta\zeta - \sum_{i=1}^n \mu_i \Delta m_i]_{t, p} = \frac{1}{2}[P]_{t, p}, \quad (40)$$

$$[\Delta\zeta + \eta\Delta t - v\Delta p]_m + [\Delta t\Delta\eta - \Delta p\Delta v]_m = \frac{1}{2}[P]_m. \quad (41)$$

Bearing in mind the fact that

$$[\Delta t\Delta\eta - \Delta p\Delta v]_m = [P]_m, \quad (42)$$

we get at once the following conditions: <sup>1</sup>

$$[\Delta\zeta - \sum_{i=1}^n \mu_i \Delta m_i]_{t, p} > 0, \quad (43)$$

$$[\Delta\zeta + \eta\Delta t - v\Delta p]_m < 0. \quad (44)$$

By a demonstration similar to those employed for  $\psi$  and for  $\chi$ , it can be shown that conditions 43 and 44 are equivalent to the condition of stability 9.

Interesting results are obtained if we apply the general criteria to the special case of a homogeneous phase of constant

<sup>1</sup> l. c. p. 166.

mass and invariable composition. Inequalities 6, 23, 27, 34, 36 and 44 give us the conditions

$$[\Delta\epsilon - t\Delta\eta + p\Delta v]_m > 0; \quad (45)$$

$$[\Delta\psi + p\Delta v]_{t,m} > 0, \quad [\Delta\psi + \eta\Delta t]_{v,m} < 0; \quad (46)$$

$$[\Delta\chi - t\Delta\eta]_{p,m} > 0, \quad [\Delta\chi - v\Delta p]_{\eta,m} < 0; \quad (47)$$

$$[\Delta\xi + \eta\Delta t - v\Delta p]_m < 0. \quad (48)$$

In 45 let us replace  $\Delta\epsilon$  by the value obtained from equation 2 by making the  $m$ 's constant. If, in addition, we make use of equations 4 and replace the symbol  $f$  by  $\epsilon$ , we get as the condition of stability

$$\frac{\partial^2 \epsilon}{\partial \eta^2} \Delta \eta^2 + 2 \frac{\partial^2 \epsilon}{\partial \eta \partial v} \Delta \eta \Delta v + \frac{\partial^2 \epsilon}{\partial v^2} \Delta v^2 > 0. \quad (49)$$

This, of course, is a particular case of the fundamental assumption 3. The necessary and sufficient conditions that this inequality be verified for all values of  $\Delta\eta$  and  $\Delta v$  are

$$\frac{\partial^2 \epsilon}{\partial \eta^2} > 0, \quad \frac{\partial^2 \epsilon}{\partial \eta^2} \frac{\partial^2 \epsilon}{\partial v^2} - \left( \frac{\partial^2 \epsilon}{\partial \eta \partial v} \right)^2 > 0. \quad (50)$$

From these conditions it follows that

$$\frac{\partial^2 \epsilon}{\partial v^2} > 0. \quad (51)$$

In like manner, if we consider  $\psi$  as a function of  $t$  and  $v$ , we may replace  $\Delta\psi$  in the first of conditions 46 by

$$\frac{\partial \psi}{\partial v} \Delta v + \frac{1}{2} \frac{\partial^2 \psi}{\partial v^2} \Delta v^2,$$

and in the second of these conditions by

$$\frac{\partial \psi}{\partial t} \Delta t + \frac{1}{2} \frac{\partial^2 \psi}{\partial t^2} \Delta t^2.$$

If we make use of the fact that

$$-p = \frac{\partial \psi}{\partial v}, \quad -\eta = \frac{\partial \psi}{\partial t},$$

conditions 46 reduce to<sup>1</sup>

$$\frac{\partial^2 \psi}{\partial v^2} > 0, \quad \frac{\partial^2 \psi}{\partial t^2} < 0. \quad (52)$$

<sup>1</sup> I. c. p. 165.

As a consequence of these we have

$$\frac{\partial^2 \psi}{\partial t^2} \frac{\partial^2 \psi}{\partial v^2} - \left( \frac{\partial^2 \psi}{\partial t \partial v} \right)^2 < 0. \quad (53)$$

If we regard  $\chi$  as a function of  $p$  and  $\eta$ , and observe that

$$t = \frac{\partial \chi}{\partial \eta}, \quad v = \frac{\partial \chi}{\partial p},$$

conditions 47 reduce to

$$\frac{\partial^2 \chi}{\partial \eta^2} > 0, \quad \frac{\partial^2 \chi}{\partial p^2} < 0, \quad (54)$$

from which follows at once

$$\frac{\partial^2 \chi}{\partial p^2} \frac{\partial^2 \chi}{\partial \eta^2} - \left( \frac{\partial^2 \chi}{\partial p \partial \eta} \right)^2 < 0. \quad (55)$$

Finally, if we consider  $\zeta$  as a function of  $t$  and  $p$  and make use of the relations

$$-\eta = \frac{\partial \zeta}{\partial t}, \quad v = \frac{\partial \zeta}{\partial p},$$

condition 48 reduces to

$$\frac{\partial^2 \zeta}{\partial t^2} \Delta t^2 + 2 \frac{\partial^2 \zeta}{\partial t \partial p} \Delta t \Delta p + \frac{\partial^2 \zeta}{\partial p^2} \Delta p^2 < 0. \quad (56)$$

The necessary and sufficient conditions for this inequality to hold are

$$\frac{\partial^2 \zeta}{\partial t^2} < 0, \quad \frac{\partial^2 \zeta}{\partial t^2} \frac{\partial^2 \zeta}{\partial p^2} - \left( \frac{\partial^2 \zeta}{\partial t \partial p} \right)^2 > 0, \quad (57)$$

from which follows at once

$$\frac{\partial^2 \zeta}{\partial p^2} < 0. \quad (58)$$

Trevor has recently given<sup>1</sup> an interesting method of obtaining the conditions 52, 53, 54, 55, 57 and 58, which here appear as special cases of Gibbs's general criteria of stability.

*New York, April 2, 1904.*

<sup>1</sup> Jour. Phys. Chem. 8, 83 (1904).

# CALCIUM SULPHATE IN AQUEOUS SOLUTIONS OF POTASSIUM AND SODIUM SULPHATES<sup>1</sup>

BY F. K. CAMERON AND J. F. BREAZEALE

This study of the solubility of calcium sulphate, or gypsum, is in continuation of the series on the solubility of this substance in solutions of various electrolytes reported in several earlier communications from this laboratory. The solubility in solutions of sodium sulphate at 22° C,<sup>2</sup> has already been given and is here again given for 25° C, with more points on the solubility curve. The solubility of calcium sulphate in potassium sulphate was made especially interesting by the formation of the so-called double salt,  $\text{CaK}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ . This double sulphate of potassium and calcium was first prepared by Phillips, and later shown to be identical with the double sulphate,  $\text{CaK}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ , found together with sylvine, KCl, in Kalusz, and formerly called Kaluszcite.<sup>3</sup> Later, on account of this relation to polyhalite, it was called syngenite. Ditte,<sup>4</sup> and more recently van 't Hoff and Wilson<sup>5</sup> have prepared this compound. Van 't Hoff and Wilson determined the composition of the solution in equilibrium with both calcium sulphate and syngenite at 25° C, and applied these data to determining the conditions governing the formation of syngenite.

## Calcium Sulphate and Potassium Sulphate

All the solubility determinations here described were made at 25° C and the method of procedure was practically the same in all cases. A series of bottles was filled with solutions of

<sup>1</sup> Published by permission of the Secretary of Agriculture.

<sup>2</sup> Jour. Phys. Chem. 5, 643 (1901); and Bulletin No. 18, p. 51, Division of Soils, U. S. Dept. of Agric., 1901.

<sup>3</sup> See Jahresb. Fortsch. Chem. 1872, 1142.

<sup>4</sup> Comptes rendus, 84, 86 (1877).

<sup>5</sup> Sitzungsber. Akad. Wiss. Berlin, 1900, 1142.

varying concentrations with respect to the more soluble salt, and an excess of calcium sulphate added to each. They were then allowed to stand twelve to fourteen days with frequent shaking, and finally allowed to settle for several days in the thermostat kept constant at  $25^{\circ}$  C. Portions of the solution were withdrawn from time to time and analyzed to determine when final equilibrium had been established. In order to ensure accurate data in this respect, in one series the solutions were heated for several hours at  $65^{\circ}$  C, and then kept in the constant temperature bath for fifteen days. Another series stood for some days at room temperature (about  $22^{\circ}$  C) and was then placed in the constant temperature bath for fifteen days. The agreement between the results from the two series was quite satisfactory and showed beyond reasonable doubt that final equilibrium conditions can be obtained in both cases. When equilibrium has been established as above described, fifty cubic centimeters were withdrawn, carefully weighed and the calcium estimated by precipitating as calcium oxalate and weighing as oxide in the usual manner. The effect of the presence of the relatively large quantity of potassium sulphate on the precipitate was tested in a separate set of experiments and was found to be so slight as to be safely negligible. In the higher concentrations of potassium sulphate the precipitate had to be washed very thoroughly to remove the excessive amount of salt, but the calcium oxalate itself was influenced very little, quantitatively. The potassium sulphate was determined by evaporating another portion of the solution to dryness and subtracting the weight of calcium sulphate found by analysis from the weight of the residue. All results are expressed in grams per liter of solutions, although the weight of a liter of the solution is also given in each case, making it possible to compute the solubility on the basis of mass of solvent instead of volume of solution. The results of a preliminary series were as follows :

## Calcium Sulphate in Solutions of Potassium Sulphate

## Preliminary Series

Weight of 1000 cc. of solution	Grams $K_2SO_4$ per liter	Grams $CaSO_4$ per liter
1003.61	4.88	1.601
1007.54	9.86	1.504
1015.54	19.71	1.534
1022.82	29.72	1.582
1032.18	41.91	1.073
1046.28	54.25	0.551
1060.35	80.04	0.398
1075.54	99.68	0.252

A second and more carefully determined series gave the following results :

## Calcium Sulphate in Solutions of Potassium Sulphate

Weight of 1000 cc. of solution	Grams $K_2SO_4$ per liter	Grams $CaSO_4$ per liter
1003.80	5.09	1.563
1007.54	9.85	1.446
1015.15	19.57	1.485
1022.86	28.35	1.553
1023.64	30.66	1.587
1024.14	31.15	1.549
1026.92	35.19	1.257
1027.32	35.79	1.213
1030.62	40.53	0.970
1072.41	96.00	0.257

A graphic representation of both series is given in the accompanying figure. The grams of calcium sulphate per liter of solution are given as ordinates and the grams of potassium sulphate as abscissæ.\* It is evident that we are dealing here with two intersecting curves. The upper of these two curves gives the solubility of calcium sulphate in solutions of potassium sulphate of varying concentrations, and the lower curve the solubility of the syngenite, which forms in solutions of concentrations of potassium sulphate greater than about 32 grams per



liter. The first curve shows the conditions of concentration for equilibrium between potassium sulphate and calcium sulphate when the solution is in contact with calcium sulphate or gyp-

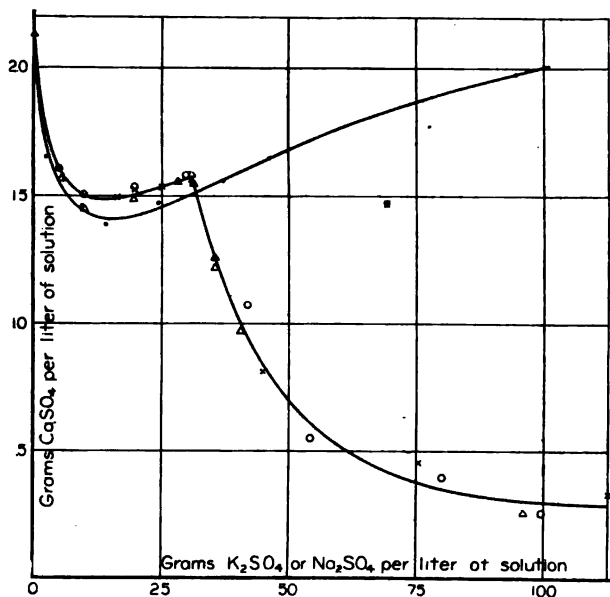


Fig. 1

- Preliminary calcium sulphate — potassium sulphate series.
- △ Calcium sulphate — potassium sulphate series.
- × Syngenite — potassium sulphate series.
- Calcium sulphate — sodium sulphate series.

sum as solid phase and the second curve the conditions with syngenite as solid phase. The intersection of the two curves gives the stable triple point where the solution is in equilibrium with both gypsum and syngenite as solid phases. This triple point is lower in respect to calcium sulphate than is found by van't Hoff and Wilson.<sup>1</sup> To test further the position of the triple point the procedure followed by these investigators was used, and the results obtained show that the values for the triple point as found by extrapolation on the curves here given are substantially correct.

<sup>1</sup> loc. cit.

	Grams per liter of solution $K_2SO_4$	Grams per liter of solution $CaSO_4$
By direct determination	32.47	1.582
By extrapolation	32.00	1.585

#### Syngenite and Potassium Sulphate

Syngenite was prepared by dissolving 120 grams of potassium sulphate in 1000 cc of water and to this was added a solution containing 20 grams of anhydrous calcium chloride in 100 cc of water. After standing some time the precipitated magma was washed with 85 percent alcohol, and finally with ordinary alcohol, until free from chlorides. This syngenite was then treated in the manner above described for the calcium sulphate in potassium sulphate solution. The concentrations of the resulting solutions in potassium sulphate and calcium sulphate are given below :

#### Syngenite in Solutions of Potassium Sulphate

Weight of 1000 cc. of solution.	Grams $K_2SO_4$ per liter	Grams $CaSO_4$ per liter
1013.08	16.31	1.495
1015.78	19.87	1.529
1020.01	25.01	1.537
1024.54	30.83	1.565
1036.82	46.99	0.810
1058.10	75.45	0.451
1085.91	112.87	0.330

In the first four determinations the syngenite was completely decomposed, gypsum was formed and remained as solid phase; the corresponding amounts of potassium sulphate passed into solution and increased the concentration with respect to this salt. Beyond the fourth determination the concentration with respect to potassium sulphate was sufficient for the existence of the syngenite in the solid phase. The results are indicated by crosses in the accompanying figure and will be seen to fall on the curve plotted from the results already given.

#### Calcium Sulphate and Sodium Sulphate

The solubility curve for gypsum in solutions of varying

concentration of sodium sulphate at 22° C as formerly determined in this laboratory<sup>1</sup> is similar in many respects to the corresponding curve for solutions of potassium sulphate. It was deemed advisable, however, to obtain the curve for solution of sodium sulphate at 25° C in order to establish this similarity with certainty. The figures obtained are given in the following table, and are illustrated in part in the figure.

Calcium Sulphate in Solutions of Sodium Sulphate

Weight of 1000 cc. of solution	Grams $\text{Na}_2\text{SO}_4$ per liter	Grams $\text{CaSO}_4$ per liter
1001.26	2.390	1.650
1007.59	9.535	1.457
1011.45	14.132	1.388
1020.46	24.369	1.471
1031.48	36.979	1.563
1039.12	46.150	1.650
1079.47	94.220	1.980
1096.47	115.084	2.096
1142.66	146.612	2.234
1176.47	205.105	2.503
1212.00	257.100	2.650

With increasing concentration of the more soluble salt, there is at first a decrease in the solubility of the calcium salt, such as would be indicated by the electrolytic dissociation hypothesis; and then a regular increase which might be explained by assuming the formation of ionic complexes in the solution by chemical union between the solvent and one or more of the solutes, or, by a change in the density of the solvent. Criteria are unfortunately yet wanting to enable us to discriminate between these suggestions. The principal difference between the two curves is that the one representing solutions of sodium sulphate does not end with the appearance of a solid double salt, none being formed at 25° C until the solution is saturated with respect to sodium sulphate decahydrate.<sup>2</sup>

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U. S. Department of Agriculture,  
Washington, D. C.*

<sup>1</sup> loc. cit.

<sup>2</sup> Van 't Hoff and Chiaraviglio, Sitzungsber. Akad. Wiss. Berlin, 1899, 817.

# THE SLOPE OF THE VAPORIZATION NEUTRAL CURVE

BY J. E. TREVOR

## Introductory : The Neutral Curve

Writing  $v_1, v_2, \eta_1, \eta_2, M_1, M_2$  for the specific volumes, the specific entropies, and the masses, of coexistent phases of liquid and vapor of a one-component system of total volume  $V$ , entropy  $H$ , and mass  $M$ , we have

$$V = (M - M_2) \cdot v_1 + M_2 \cdot v_2$$

$$H = (M - M_2) \cdot \eta_1 + M_2 \cdot \eta_2$$

From these equations follow, in the state-variables  $\theta, M_2$ ,

$$(1) \quad dV = \left( (M - M_2) \frac{dv_1}{d\theta} + M_2 \frac{dv_2}{d\theta} \right) d\theta + (v_2 - v_1) dM_2$$

$$(2) \quad dH = \frac{(M - M_2) \cdot c_1 + M_2 \cdot c_2}{\theta} d\theta + \frac{r}{\theta} dM_2,$$

and, in the state-variables  $p, M_2$ ,

$$(3) \quad dV = \left( (M - M_2) \frac{dv_1}{dp} + M_2 \frac{dv_2}{dp} \right) dp + (v_2 - v_1) dM_2$$

$$(4) \quad dH = \frac{(M - M_2) \cdot c'_1 + M_2 \cdot c'_2}{\theta} dp + \frac{r}{\theta} dM_2,$$

in which equations  $p, \theta, r$  denote pressure, absolute temperature, and the specific heat of vaporization, and the  $c$ 's denote the thermal coefficients

$$c_1 = \theta \frac{d\eta_1}{d\theta}, \quad c_2 = \theta \frac{d\eta_2}{d\theta}, \quad c'_1 = \theta \frac{d\eta_1}{dp}, \quad c'_2 = \theta \frac{d\eta_2}{dp}.$$

Here  $c_1, c_2$  are the specific heats of 'saturated' liquid and vapor. Successive elimination of  $dM_2, d\theta$  between (1), (2), and of  $dM_2, dp$  between (3), (4), yields, further

$$(5) \quad \frac{\partial(V, H)}{\partial(\theta, M_2)} d\theta = \frac{r}{\theta} dV - (v_2 - v_1) dH$$

$$(6) \quad \frac{\partial(V, H)}{\partial(\theta, M_2)} dM = - \frac{(M - M_2) \cdot c_1 + M_2 \cdot c_2}{\theta} dV + \left( (M - M_2) \frac{dv_1}{d\theta} + M_2 \frac{dv_2}{d\theta} \right) dH$$

$$(7) \frac{\partial(V, H)}{\partial(\rho, M_2)} d\rho = \frac{r}{\theta} dV - (v_2 - v_1) dH$$

$$(8) \frac{\partial(V, H)}{\partial(\rho, M_2)} dM = - \frac{(M - M_2) \cdot c_1' + M_2 \cdot c_2'}{\theta} dV + \left( (M - M_2) \frac{dv_1}{d\rho} + M_2 \frac{dv_2}{d\rho} \right) dH.$$

Introducing the abbreviated notation

$$\frac{\partial(V, H)}{\partial(\theta, M_2)} = J_1(\theta, M_2), \quad \frac{\partial(V, H)}{\partial(\rho, M_2)} = J_2(\rho, M_2),$$

for the jacobians, we obtain from the foregoing equations the following expressions for the first derivatives of the derived functions  $\rho, \theta, V, H, M_2$ .

$$\left( \frac{\partial V}{\partial M_2} \right)_\theta = v_2 - v_1$$

$$\left( \frac{\partial H}{\partial M_2} \right)_\theta = -\frac{r}{\theta}$$

$$\left( \frac{\partial H}{\partial V} \right)_\theta = \frac{1}{\theta} \frac{r}{v_2 - v_1}$$

$$\left( \frac{\partial V}{\partial M_2} \right)_\rho = v_2 - v_1$$

$$\left( \frac{\partial H}{\partial M_2} \right)_\rho = \frac{r}{\theta}$$

$$\left( \frac{\partial H}{\partial V} \right)_\rho = \frac{1}{\theta} \frac{r}{v_2 - v_1}$$

$$\left( \frac{\partial \theta}{\partial H} \right)_v = -\frac{v_2 - v_1}{J_1}$$

$$\left( \frac{\partial \rho}{\partial H} \right)_v = -\frac{v_2 - v_1}{J_2}$$

$$\left( \frac{\partial M_2}{\partial \theta} \right)_v = -\frac{(M - M_2) \frac{dv_1}{d\theta} + M_2 \frac{dv_2}{d\theta}}{v_2 - v_1}$$

$$\left( \frac{\partial M_2}{\partial \rho} \right)_v = -\frac{(M - M_2) \frac{dv_1}{d\rho} + M_2 \frac{dv_2}{d\rho}}{v_2 - v_1}$$

$$\begin{aligned} \left( \frac{\partial M_2}{\partial H} \right)_v &= \frac{1}{J_1} \left( (M - M_2) \frac{dv_1}{d\theta} + M_2 \frac{dv_2}{d\theta} \right) \\ &= \frac{1}{J_2} \left( (M - M_2) \frac{dv_1}{d\rho} + M_2 \frac{dv_2}{d\rho} \right) \end{aligned}$$

$$\left( \frac{\partial \theta}{\partial V} \right)_H = \frac{1}{J_1} \frac{r}{\theta}$$

$$\left( \frac{\partial \rho}{\partial V} \right)_H = \frac{1}{J_2} \frac{r}{\theta}$$

$$\left( \frac{\partial M_2}{\partial \theta} \right)_H = -\frac{(M - M_2) \cdot c_1 + M_2 \cdot c_2}{r}$$

$$\left( \frac{\partial M_2}{\partial \rho} \right)_H = -\frac{(M - M_2) \cdot c_1' + M_2 \cdot c_2'}{r}$$

$$\begin{aligned} \left( \frac{\partial M_2}{\partial V} \right)_H &= -\frac{1}{J_1} \frac{(M - M_2) \cdot c_1 + M_2 \cdot c_2}{\theta} \\ &= -\frac{1}{J_2} \frac{(M - M_2) \cdot c_1' + M_2 \cdot c_2'}{\theta} \end{aligned}$$

$$\left( \frac{\partial V}{\partial \theta} \right)_{M_2} = (M - M_2) \frac{dv_1}{d\theta} + M_2 \frac{dv_2}{d\theta}$$

$$\left( \frac{\partial V}{\partial \rho} \right)_{M_2} = (M - M_2) \frac{dv_1}{d\rho} + M_2 \frac{dv_2}{d\rho}$$

$$\left( \frac{\partial H}{\partial \theta} \right)_{M_2} = \frac{(M - M_2) \cdot c_1 + M_2 \cdot c_2}{\theta}$$

$$\left( \frac{\partial H}{\partial \rho} \right)_{M_2} = \frac{(M - M_2) \cdot c_1' + M_2 \cdot c_2'}{\theta}$$

$$\begin{aligned} \left( \frac{\partial H}{\partial V} \right)_{M_2} &= \frac{1}{\theta} \frac{(M - M_2) \cdot c_1 + M_2 \cdot c_2}{(M - M_2) \frac{dv_1}{d\theta} + M_2 \frac{dv_2}{d\theta}} \\ &= \frac{1}{\theta} \frac{(M - M_2) \cdot c_1' + M_2 \cdot c_2'}{(M - M_2) \frac{dv_1}{d\rho} + M_2 \frac{dv_2}{d\rho}} \end{aligned}$$

We also have

$$\begin{aligned}\frac{dp}{d\theta} &= \left(\frac{\partial V}{\partial \theta}\right)_{M_2} : \left(\frac{\partial V}{\partial p}\right)_{M_2} = \left(\frac{\partial H}{\partial \theta}\right)_{M_2} : \left(\frac{\partial H}{\partial p}\right)_{M_2} = \left(\frac{\partial p}{\partial H}\right)_V : \left(\frac{\partial \theta}{\partial H}\right)_V \\ &= \left(\frac{\partial M_2}{\partial \theta}\right)_V : \left(\frac{\partial M_2}{\partial p}\right)_V = \left(\frac{\partial M_2}{\partial \theta}\right)_H : \left(\frac{\partial M_2}{\partial p}\right)_H = \left(\frac{\partial p}{\partial V}\right)_H : \left(\frac{\partial \theta}{\partial V}\right)_H\end{aligned}$$

either of which sets yields

$$(9) \quad \frac{dp}{d\theta} = \frac{(M - M_2) \frac{dv_1}{d\theta} + M_2 \frac{dv_2}{d\theta}}{(M - M_2) \frac{dv_1}{dp} + M_2 \frac{dv_2}{dp}} = \frac{(M - M_2) \cdot c_1 + M_2 \cdot c_2}{(M - M_2) \cdot c_1' + M_2 \cdot c_2'} = \frac{J_1}{J_2}.$$

The rates of adiabatic evaporation, replacing the expression in the  $c'$ 's in the second case by the expression in the  $c$ 's, by means of (9), are

$$\begin{aligned}(10) \quad \left(\frac{\partial M_2}{\partial \theta}\right)_H &= - \frac{(M - M_2) \cdot c_1 + M_2 \cdot c_2}{r} \\ \left(\frac{\partial M_2}{\partial p}\right)_H &= - \frac{(M - M_2) \cdot c_1 + M_2 \cdot c_2}{r} \cdot \frac{d\theta}{dp} \\ \left(\frac{\partial M_2}{\partial V}\right)_H &= - \frac{(M - M_2) \cdot c_1 + M_2 \cdot c_2}{\theta} \cdot \frac{1}{J_1}.\end{aligned}$$

It is well known that the signs of these rates depend on the sign of the expression

$$(M - M_2) \cdot c_1 + M_2 \cdot c_2.$$

For, in these formulations, if we omit consideration of the critical point,

$$r > 0, \quad \frac{d\theta}{dp} > 0;$$

and, further, because of the tabulated equation

$$\left(\frac{\partial \theta}{\partial H}\right)_V = - \frac{v_2 - v_1}{J_1},$$

it appears that

$$J_1 = - (v_2 - v_1) : \left(\frac{\partial \theta}{\partial H}\right)_V = < 0.$$

Incidentally, from (9),

$$J_2 = J_1 : \frac{dp}{d\theta},$$

it is seen to follow that  $J_2$  is also always negative.

From equations (10) it thus appears that

When  $\frac{M - M_2}{M_1} > \frac{-c_2}{c_1}$ , adiabatic expansion induces evaporation,

When  $\frac{M - M_2}{M_1} < \frac{-c_2}{c_1}$ , adiabatic expansion induces condensation,

When  $\frac{M - M_2}{M_1} = \frac{-c_2}{c_1}$ , adiabatic expansion is isopsychric,

curves of constant  $M_2$ , following Natanson,<sup>1</sup> being termed 'isopsychric curves.'

In any diagrammatic representation, then, the 'neutral curve' (Natanson)

$$\frac{M - M_2}{M_1} = \frac{-c_2}{c_1}$$

separates the two-phase field into two portions, in one of which adiabatic expansion induces evaporation, in the other condensation. And since adiabatic expansion is isopsychric at points on the neutral curve, this curve is the locus of the points of mutual tangency of the adiabatics and isopsychrics.<sup>2</sup>

### The Slopes of the Neutral Curve

Let us now seek expressions for the slopes of the neutral curve in the various diagrams formed by taking as rectangular coordinates any pair of state-variables from either of the sets

$$\begin{aligned} p, V, H, M_1; \\ \theta, V, H, M_1. \end{aligned}$$

For example, let it be required to find the slope of the locus of the points of mutual tangency of the families

$$\begin{aligned} p &= p(V, H) \\ p &= p(V, M_1) \end{aligned}$$

of adiabatics and isopsychrics in the  $p, V$ -diagram. In the general problem, let

<sup>1</sup> Natanson. Bull. Acad. Sci. Cracovie, 1895, 132 (1895). Reprinted in Jour. de Phys. (3) 4, 305 (1895).

<sup>2</sup> Raveau. Jour. de Phys. (3) 1, 461 (1892). Natanson. l. c.

$$(11) \quad y = \phi(x, a)$$

$$(12) \quad y = \psi(x, b)$$

be the equations of two families of curves,  $a$ ,  $b$  being variable parameters. The equation of the locus of the points of mutual tangency is to be obtained by elimination of  $a$ ,  $b$  between (11), (12) and the condition

$$(13) \quad \frac{\partial \phi}{\partial x} = \frac{\partial \psi}{\partial x};$$

i. e., the equation of the locus is (13), wherein  $a$ ,  $b$  are understood as expressed by their values as functions of  $x$ ,  $y$  obtained from (11), (12).

The slope  $dy/dx$  of the locus is similarly to be obtained by differentiating (13) with regard to  $x$ , and eliminating the derivatives of  $a$ ,  $b$  by means of (11), (12).<sup>1</sup>

The functions  $\partial \phi / \partial x$  and  $\partial \psi / \partial x$  are, then, functions

$$f_1\{x, a(x, y(x))\}, \quad f_2\{x, b(x, y(x))\};$$

so differentiation of (13) with regard to  $x$  yields

$$\begin{aligned} \frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial x \partial a} \left( \frac{\partial a}{\partial x} + \frac{\partial a}{\partial y} \frac{\partial y}{\partial x} \right) \\ = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial x \partial b} \left( \frac{\partial b}{\partial x} + \frac{\partial b}{\partial y} \frac{\partial y}{\partial x} \right). \end{aligned}$$

From (11), (12) we obtain, for the derivatives of  $a$ ,  $b$ ,

$$\begin{aligned} \frac{\partial a}{\partial x} &= - \frac{\partial \phi}{\partial x} : \frac{\partial \phi}{\partial a} & \frac{\partial b}{\partial x} &= - \frac{\partial \psi}{\partial x} : \frac{\partial \psi}{\partial b} \\ \frac{\partial a}{\partial y} &= 1 : \frac{\partial \phi}{\partial a} & \frac{\partial b}{\partial y} &= 1 : \frac{\partial \psi}{\partial b} \end{aligned}$$

Substituting these values, and solving for the slope  $dy/dx$ , we find

$$\frac{dy}{dx} = \frac{\frac{\partial \psi}{\partial b} \frac{\partial(\phi, \partial \phi / \partial x)}{\partial(x, a)} - \frac{\partial \phi}{\partial a} \frac{\partial(\psi, \partial \psi / \partial x)}{\partial(x, b)}}{\frac{\partial \psi}{\partial b} \frac{\partial^2 \phi}{\partial x \partial a} - \frac{\partial \phi}{\partial a} \frac{\partial^2 \psi}{\partial x \partial b}},$$

or, in an obvious notation,

<sup>1</sup> I owe this suggestion to my colleague, Prof. James McMahon.



$$(14) \quad \frac{dy}{dx} = \frac{\frac{J(\phi)}{\phi_2} - \frac{J(\psi)}{\psi_2}}{\frac{\phi_{12}}{\phi_2} - \frac{\psi_{12}}{\psi_2}}.$$

This equation (14) may be regarded as the general solution of the problem; yet we shall obtain more interesting special results if we immediately differentiate the equation of the neutral curve,

$$(M - M_2) \cdot c_1 + M_2 \cdot c = 0.$$

The most natural procedure will be to find directly expressions for the slopes

$$\frac{dM_2}{dp}, \quad \frac{dM_2}{d\theta}, \quad \frac{dV}{dp}, \quad \frac{dV}{d\theta}, \quad \frac{dH}{dp}, \quad \frac{dH}{d\theta},$$

and thereupon to express the remaining slopes by means of ratios of these results. It will be convenient to write the equation of the neutral curve in the form

$$(15) \quad \begin{aligned} M_2 &= M \frac{c_1}{c_1 - c_2} \\ &= MC. \end{aligned}$$

We now proceed to execute this programme.

In the state-variables  $p, M_2$ , and in the variables  $\theta, M_2$ , the equation of the neutral curve is

$$M_2 = M \cdot C(p), \quad M_2 = M \cdot C(\theta),$$

whence

$$(16) \quad \frac{1}{M} \frac{dM_2}{dp} = \frac{dC}{dp}, \quad \frac{1}{M} \frac{dM_2}{d\theta} = \frac{dC}{d\theta}.$$

In the state-variables  $p, V$ , and in the variables  $\theta, V$ , we have

$$\begin{aligned} M_2(p, V) &= M \cdot C(p) \\ M_2(\theta, V) &= M \cdot C(\theta); \end{aligned}$$

whence

$$\begin{aligned} \left( M \frac{dC}{dp} - \frac{\partial M_2}{\partial p} \right) dp &= \frac{\partial M_2}{\partial V} dV \\ \left( M \frac{dC}{d\theta} - \frac{\partial M_2}{\partial \theta} \right) d\theta &= \frac{\partial M_2}{\partial V} dV. \end{aligned}$$

Taking the partial derivatives from the table, and eliminating  $M_2$ ,

$$\frac{\partial M_2}{\partial p} = -M \frac{(1-C) \frac{dv_1}{dp} + C \frac{dv_2}{dp}}{v_2 - v_1}$$

$$\frac{\partial M_2}{\partial \theta} = -M \frac{(1-C) \frac{dv_1}{d\theta} + C \frac{dv_2}{d\theta}}{v_2 - v_1}$$

$$\left(\frac{\partial M_2}{\partial V}\right)_p = \left(\frac{\partial M_2}{\partial V}\right)_\theta = \frac{1}{v_2 - v_1};$$

which convert the differential equations to

$$(17) \quad \begin{cases} \frac{1}{M} \frac{dV}{dp} = (v_2 - v_1) \frac{dC}{dp} + (1-C) \frac{dv_1}{dp} + C \frac{dv_2}{dp} \\ \frac{1}{M} \frac{dV}{d\theta} = (v_2 - v_1) \frac{dC}{d\theta} + (1-C) \frac{dv_1}{d\theta} + C \frac{dv_2}{d\theta} \\ \frac{1}{M} \frac{dV}{dp} = \frac{d}{dp} (Cv_2 - (C-1)v_1) \\ \frac{1}{M} \frac{dV}{d\theta} = \frac{d}{d\theta} (Cv_2 - (C-1)v_1) \end{cases}$$

In the state-variables  $p, H$ , and in the variables  $\theta, H$ , we have

$$M_2(p, H) = M \cdot C(p)$$

$$M_2(\theta, H) = M \cdot C(\theta);$$

whence

$$\left(M \frac{dC}{dp} = \frac{\partial M_2}{\partial p}\right) dp = \frac{\partial M_2}{\partial H} dH$$

$$\left(M \frac{dC}{d\theta} = \frac{\partial M_2}{\partial \theta}\right) d\theta = \frac{\partial M_2}{\partial H} dH.$$

Taking the partial derivatives from the table,

$$\frac{\partial M_2}{\partial p} = 0, \quad \frac{\partial M_2}{\partial \theta} = 0, \quad \left(\frac{\partial M_2}{\partial H}\right)_p = \left(\frac{\partial M_2}{\partial H}\right)_\theta = \frac{\theta}{r};$$

which convert the differential equations to

$$M \frac{dC}{dp} dp = \frac{\theta}{r} dH, \quad M \frac{dC}{d\theta} d\theta = \frac{\theta}{r} dH;$$

which yield

$$(18) \quad \frac{1}{M} \frac{dH}{dp} = \frac{r}{\theta} \frac{dC}{dp}, \quad \frac{1}{M} \frac{dH}{d\theta} = \frac{r}{\theta} \frac{dC}{d\theta}.$$

The remaining formulations are to be obtained from those just deduced, by means of the relations

$$\begin{aligned}\frac{dH}{dM_2} &= \frac{dH}{dp} : \frac{dM_2}{dp} = \frac{dH}{d\theta} : \frac{dM_2}{d\theta} \\ \frac{dV}{dM_2} &= \frac{dV}{dp} : \frac{dM_2}{dp} = \frac{dV}{d\theta} : \frac{dM_2}{d\theta} \\ \frac{dV}{dH} &= \frac{dV}{dp} : \frac{dH}{dp} = \frac{dV}{d\theta} : \frac{dH}{d\theta}\end{aligned}$$

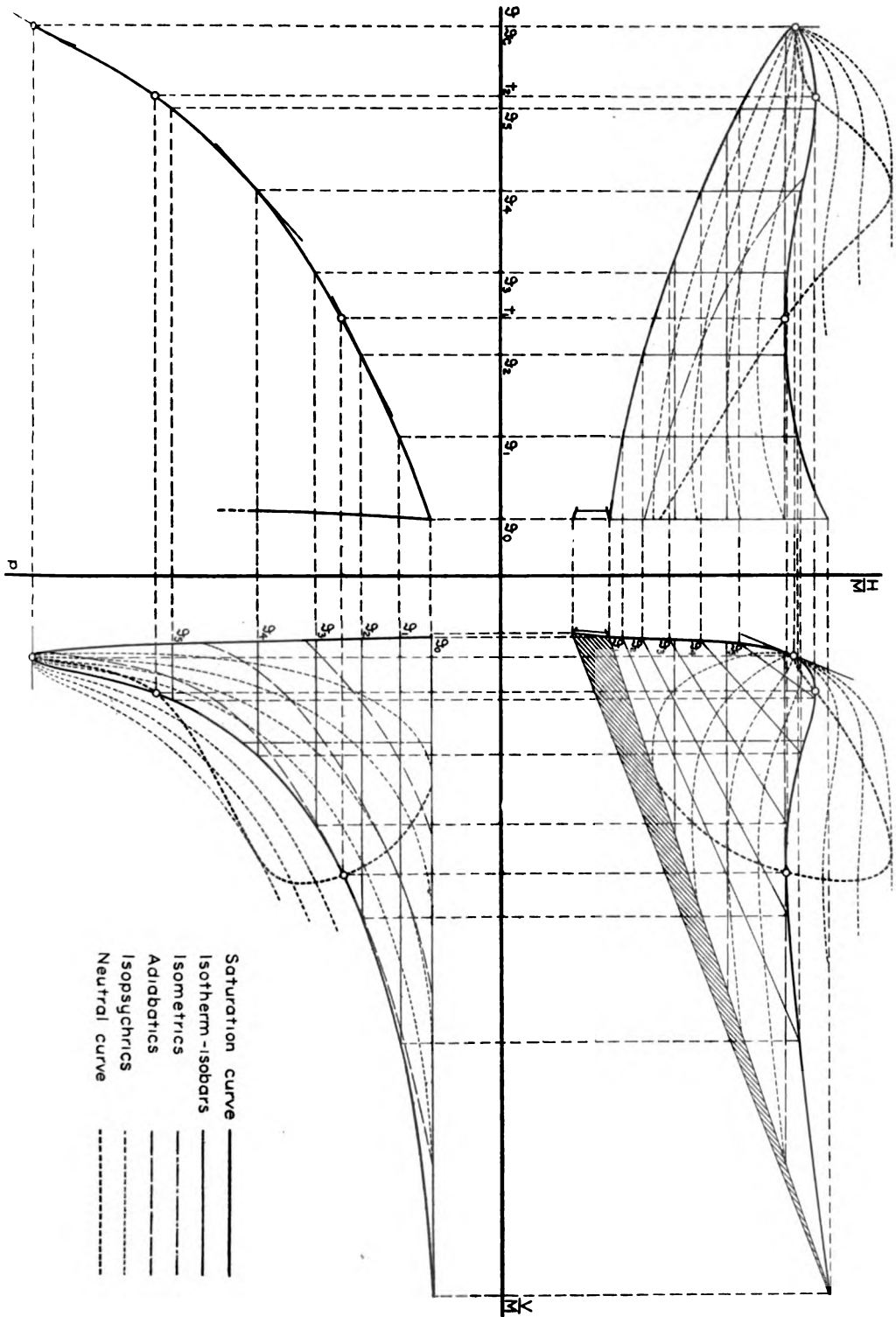
The formulations of  $dV/dM_2$  and  $dV/dH$  may be directly obtained, as in the foregoing, by differentiation of the equations

$$\begin{aligned}M_2 &= M \cdot C(\theta(V, M_2)) \\ M_2(V, H) &= M \cdot C(\theta(V, H)).\end{aligned}$$

In the case of  $dH/dM_2$ , the direct calculation leads to an indeterminate result.

Collecting the results, we have the following equations for the slope of the neutral curve in the various plane diagrams mentioned :

$$\begin{aligned}\frac{I}{M} \frac{dM_2}{dp} &= \frac{d}{dp} \frac{c_1}{c_1 - c_2} & \left| & \frac{I}{M} \frac{dM_2}{d\theta} = \frac{d}{d\theta} \frac{c_1}{c_1 - c_2} \right. \\ \frac{I}{M} \frac{dH}{dp} &= \frac{r}{\theta} \cdot \frac{d}{dp} \frac{c_1}{c_1 - c_2} & \left| & \frac{I}{M} \frac{dH}{d\theta} = \frac{r}{\theta} \cdot \frac{d}{d\theta} \frac{c_1}{c_1 - c_2} \right. \\ \frac{I}{M} \frac{dV}{dp} &= \frac{d}{dp} \left( \frac{c_1}{c_1 - c_2} v_2 - \frac{c_2}{c_1 - c_2} v_1 \right) \\ \frac{I}{M} \frac{dV}{d\theta} &= \frac{d}{d\theta} \left( \frac{c_1}{c_1 - c_2} v_2 - \frac{c_2}{c_1 - c_2} v_1 \right) \\ \frac{dH}{dM_2} &= \frac{r}{\theta} \\ \frac{dV}{dM_2} &= \frac{d \left( \frac{c_1}{c_1 - c_2} v_2 - \frac{c_2}{c_1 - c_2} v_1 \right)}{d \frac{c_1}{c_1 - c_2}} \\ \frac{dV}{dH} &= \frac{\theta}{r} \frac{d \left( \frac{c_1}{c_1 - c_2} v_2 - \frac{c_2}{c_1 - c_2} v_1 \right)}{d \frac{c_1}{c_1 - c_2}}.\end{aligned}$$



Perhaps the most curious of the above results is the seventh, which may be written

$$\frac{dH}{dM_1} = \eta_2 - \eta_1.$$

This equation asserts that, at any point on the neutral curve in the two-phase field, the change of entropy per unit evaporation is the same along the neutral curve and along the isotherm.

In the case of a substance having two transition temperatures,  $\theta = t_1$  and  $\theta = t_2$ , between the triple point temperature  $\theta_0$  and the critical temperature  $\theta_c$ , the course of the neutral curve in the  $p$ , $V$ -diagram, in the  $\theta$ , $H$ -diagram, and in the  $H$ , $V$ -diagram, will be somewhat as indicated in the accompanying set of schematic diagrams. The  $p$ , $H$ -diagram and the  $\theta$ , $V$ -diagram are not included in the drawing, the form that the curve will exhibit in them being sufficiently obvious from the diagrams that are presented.

*Cornell University,  
March, 1904.*

# A MECHANICAL MODEL TO ILLUSTRATE THE GAS LAWS

BY FRANK B. KENRICK

The difficulty of getting elementary students to grasp the fundamental ideas of the gas laws, Carnot's cycle, the entropy function, etc., must have confronted every teacher of physical chemistry. The student learns all too easily that "peevee equals enartee", but the apparent simplicity of the relations and the absence of concrete conceptions and numerical examples—to say nothing of absence of interest—combine to create a state of vagueness which will often hamper his progress for years. In order to overcome this difficulty the writer has constructed a simple model which has worked admirably, not only in giving students definite conceptions of Carnot's cycle, etc., but also in awakening their interest in, and aiding them to grasp, the essential idea of the calculus.

The model described below is, of course, only one of many possible arrangements which are not difficult to invent on paper, but this one has the advantage of having been actually tried and used by students, and this seems a sufficient reason for publishing its description. It can be constructed with about a day's work by any amateur mechanic.

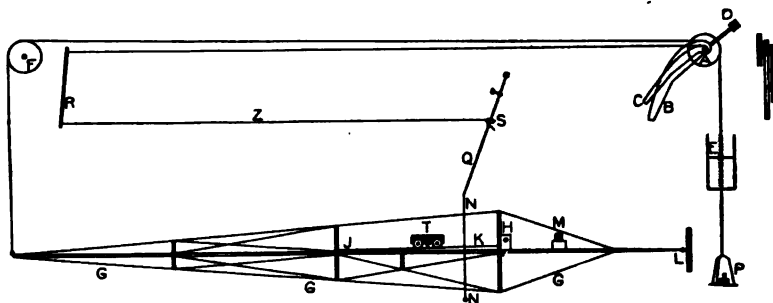


Fig. 1

It may be objected that the model is more complicated than

the laws it is intended to elucidate. To this it may be answered that if it were *not* so the students would pass it over as lightly as they do the laws themselves.

The model is set up on the vacant wall of a laboratory where students may work with it without interference from instructors. The essential part of the apparatus is a circular wooden pulley A, 20 cm in diameter, to which is fixed rigidly a wooden curve B, the co-ordinates of which are given in Table I, and which, together with the second curve (mentioned below), is exactly counterbalanced by the weight D. The curves are made of 3/8-inch pine and carry double rows of ordinary pins on the edge which act as flanges. The whole is pivoted with brass bearings on a horizontal steel pin. At a suitable point on A is fixed an iron wire (No. 24, B. & S.) which carries a pan P at its lower end. A tin cross-piece is attached to the wire at a convenient height from the ground to represent a piston, behind which is a piece of cardboard bearing a diagram of a cylinder and a millimeter scale. To the right hand end of the curve B a piece of strong thread is fastened, which passes round the curve to a pulley F, similar to A, and thence downwards to the end of the lever G, pivoted at H. This lever is made of a strip of light wood, about 4 meters long, and is braced with wire, as shown in the diagram, and also in the horizontal plane. It is counterbalanced by the weight M and is strong enough to carry a 5 kg weight at T. This weight rests on a toy wagon which may be moved along a flat board between J and K. On the edge of this board, which is in such a position that the centre of gravity of the weight remains in a line with the end of the lever and the fulcrum, is pasted a millimeter scale, numbered from the fulcrum as zero.

The curve B fulfils the condition that the length of the perpendicular from the centre of revolution to the horizontal tangent is inversely proportional to the angle through which the curve is moved. It is part of an infinite spiral, and was obtained graphically as the envelope of a suitable number of tangents. The position of the bottom of the cylinder (vol. = 0) may be found by turning the curve to the position in which the  $y$ -axis

(see table) is horizontal. This corresponds to the angle of revolution taken as zero, in drawing the curve. The distance of A from F, about 5 meters, is such that the thread remains practically horizontal.

This arrangement gives the relation between pressure, volume, and temperature,

$$pv = nRt.$$

The pressure in grams is the weight on the pan P, *plus* the weight of the pan which is 100 g. The volume is the distance of E from the bottom of the cylinder, and the absolute temperature is the distance, in millimeters, of a pointer at the centre of gravity of the wagon T from the fulcrum H. For the dimensions and weight given, the value of  $n$  is 0.000317 g-mol and the limits of volume are in the ratio of 1 to 5.

The work done in compressing the gas isothermally is equal to the work required to raise the weight T, and therefore the scale L (which is 1400 mm from the fulcrum) gives the value of  $\text{const.} \log v + \text{const.}$  If  $d$  is the reading in centimeters on this scale,

$$\text{work} = 5000 \frac{t}{1400} d \text{ g-cm.}$$

The additional restriction imposed on the variability of  $p$ ,  $v$ , and  $t$  for *adiabatic* changes is supplied by the following arrangement. To the wheel A is fixed a second curve C which fulfils the following condition :

$$s = \frac{\text{const}}{a^{k-1}},$$

where  $s$  is the horizontal movement of a tangential thread,  $a$  the angle of rotation, and  $k$  the ratio  $Cp/Cv$ .

If  $l$  is the length of the perpendicular from the centre of revolution to the horizontal tangent, then

$$l = \frac{ds}{da} = \text{const}' a^{-k},$$

and consequently it was possible to obtain this curve, graphically, exactly as in the case of the one already described. The co-



ordinates of the curve for  $k = 2$  are given in Table II.<sup>1</sup> The tangential thread<sup>2</sup> actuates the lever R and the pointer Q, made of a very light, thin glass tube properly counterbalanced, to the end of which is attached a plumb line N, N of fine cotton terminating in a small weight. Since R is at a distance of about five meters from C and Q, it is clear that the horizontal movements of the plumb line N represent the alteration of temperature for an adiabatic change of volume,  $v$ , or,

$$tv^k - 1 = \text{const.}$$

Since the pivot of Q is exactly over the zero of absolute temperature, H, the proper value may be given to the above constant for any adiabatic line by moving the connecting point S (a small piece of sheet rubber with a hole in it) up or down the glass pointer till N is opposite the pointer on the temperature wagon. To carry out an adiabatic expansion, therefore, it is simply necessary to set the pointer for the initial state by adjustment of the point S, and then to keep the temperature wagon opposite N during the alterations of pressure. It is necessary, of course, after setting up the model, to adjust the length of the fiber Z, so that at infinite volume the adiabatic pointer will be at zero. This can be done by adjusting the fiber to any length, taking two pairs of readings of temperature and volume, and calculating what correction in length will satisfy the above equation.

The co-ordinates of the curves B and C are given in the following tables. The values are expressed in centimeters. For both curves the centre of revolution is  $x = 10$ ,  $y = 12.5$  and the tangent for vol. = 0 is parallel to the  $y$ -axis.

<sup>1</sup> The value 2 was chosen rather than an actual value for some known gas, both to simplify the calculations and also to avoid the extreme slenderness of the  $p$ ,  $v$ -diagram of an actual Carnot's cycle.

<sup>2</sup> Owing to the necessary lightness of the pointer and plumb line, the "sag" even of the finest cotton introduces an error. For this reason fine glass fibers were used for working the adiabatic pointer and found quite satisfactory. They can be attached to pieces of cotton, at the two ends, by strips of gummed paper.

TABLE I. (Curve B)

$x$	$y$	$x$	$y$
10.8	8.7	4.5	17.7
10.0	8.45	5.4	19.4
9.1	8.4	6.7	21.0
8.15	8.5	8.5	22.4
7.25	8.75	11.1	23.7
6.40	9.2	14.0	24.5
5.5	9.95	18.1	24.9
4.8	10.9	23.3	24.3
4.25	11.9	30.0	22.2
3.9	13.0	38.5	17.5
3.8	14.3	49.5	8.4
4.0	16.0	57.5	0.0

TABLE II. (Curve C)

$x$	$y$	$x$	$y$
10.2	12.0	17.7	18.7
10.0	11.87	21.0	18.5
9.7	11.8	23.5	18.1
9.3	11.9	27.0	17.1
8.9	12.2	30.2	16.0
8.6	12.7	38.6	11.9
8.4	13.6	49.0	5.5
8.7	14.7	55.5	0.4
9.8	16.2	—	—
11.2	17.2	—	—
12.6	17.9	—	—
15.0	18.5	—	—

In conclusion, a few examples of the problems illustrated by the model may not be out of place.<sup>1</sup>

A Carnot's cycle process was carried out between the absolute temperatures  $483^{\circ}$  and  $360^{\circ}$ , and a number of points were plotted in pressure-volume co-ordinates on millimeter paper. The various areas were cut out, weighed, and compared with a square of paper of known size. The work gained during the cycle was calculated by the following methods:

<sup>1</sup> The numbers and calculations were supplied by two second year students, Messrs. T. B. Allen and R. A. Daly.

- (1) Weight of area enclosed by the two isothermals and two adiabatics, 0.2320 g, corresponding to 1850 g-cm.
- (2) Weights of areas representing work done during isothermal expansions at  $483^{\circ}$  and  $360^{\circ}$ , respectively,  
 0.8965 g, corresponding to 7156 g-cm  
 and 0.6697 g, " " 5346 "  
 Difference . . . . . 1810 g-cm.
- (3)  $\frac{T' - T''}{T'} Q_1 = \frac{483 - 360}{483} 7156 = \dots\dots\dots 1822 \text{ g-cm.}$
- (4)  $0.000317 R \left( 483 \log_e \frac{28.0}{16.2} - 360 \log_e \frac{37.0}{21.4} \right) = 1636 \text{ g-cm.}$

The work done during the isothermal expansion at  $483^{\circ}$ , calculated *directly* from *weight of wagon* (4855 g)  $\times$  distance raised (determined from movement of pointer, 4.13 cm, on scale L in figure) was :

$$4855 - \frac{483}{1400} \cdot 4.13 = 6916 \text{ g-cm (compare value above, 7156 g-cm.)}$$

The equality of the amounts of work done during the two adiabatic expansions is illustrated by the weights of the corresponding areas of paper :

$$0.3993 \text{ g and } 0.4045 \text{ g.}$$

The values of the constant R, calculated from various points, taken at random, from the above-mentioned curves, are

$$85310, 85190, 83710, 85150, 84740.$$

The constancy of  $pv^k$  is illustrated by the values calculated for three points on one of the adiabatics :

$$21250, 21100, 20820.$$

It will be noticed that the model is not perfect; but the same may be said of gases.

*University of Toronto,  
 Chemical Laboratory,  
 April, 1904.*

## NEW BOOKS

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**A Treatise on the Theory of Solution, Including the Phenomena of Electrolysis.** By William Cecil Dampier Whelham. 15 X 23 cm; pp. ix + 488. Cambridge: At the University Press, 1902. — There is an introductory chapter on thermodynamics; then come two chapters on the phase rule, one on solubility, and one on osmotic pressure. Vapor pressures and freezing-points are dealt with in the fifth chapter and theories of solution in the sixth. The next five chapters have the headings: electrolysis, conductivity of electrolytes, galvanic cells, contact electricity and polarization, the theory of electrolytic dissociation. The last two chapters are on diffusion in solutions and on solutions of colloids.

The book gives one the impression of having been written for the author's own satisfaction rather than to fill any distinct gap. While this makes it a little less valuable as a text-book, the freedom from shackles makes the volume more interesting to read than it might otherwise have been. There are a number of good points to be found in the book on which previous text-books have not laid the same stress. We are glad to see an account, p. 97, of Pickering's experiments with propyl alcohol and water, experiments which are very interesting as they stand and which certainly ought to be repeated. The filtration of permanganate through silica, p. 98, is valuable through its possible bearing on the existence of fresh water wells near the sea, as at Galveston and elsewhere. The peculiar structure of salt water ice, p. 145, is distinctly interesting. The remarks on the convergence temperature, p. 154, are good as far as they go and the reviewer would have welcomed a more exhaustive discussion of this point. Space could have been obtained for this by cutting out the paragraphs on the manipulation of the Beckmann freezing-point apparatus.

As was to be expected, the section on ion velocities is very complete, and it is interesting to notice that this is brought in before the discussion of the theory of electrolytic dissociation. This has the advantage of distinguishing sharply between experimental facts and the hypotheses made to account for those facts. Reed's work on the precipitation of hydrogen at lead cathodes is mentioned, p. 263; there is an excellent discussion on contact electromotive force, p. 271, and the question of the single potential difference, p. 281, is well handled, though Carveth's work appears to have been overlooked. Electrical endosmose receives a few pages and the chapter on colloids is admirable.

There are relatively few slips in the book. Sulphur and toluene form two liquid layers having a vapor pressure lying between the pressures of the pure components. Richards, Collins and Heimrod did not make a new determination of the electrochemical equivalent. They studied the current efficiencies of different types of silver voltameters. It is a pity to mention Ramsay's work on metals in mercury, p. 244, without referring to the results with sodium, barium and calcium. These mistakes are relatively unimportant. The book has a distinct character and an advanced student will do well to read it.

*Wilder D. Bancroft*

**Hypochlorite und elektrische Bleiche.** *Technisch-konstruktiver Teil.* By Viktor Engelhardt. (*Monographien über angewandte Elektrochemie, VIII. Band.*) 17 × 24 cm; pp. xiv + 275. Halle: Wilhelm Knapp, 1903. Price: paper, 12 marks. — When the bleaching takes place in the same vessel in which the halide salt is being electrolyzed, this is classed as "direct electrical bleaching", while "indirect electrical bleaching" includes all cases in which there is a transfer of the electrolyzed solution or of the products of electrolysis. Three types of indirect electrical bleaching are recognized. In one no diaphragm is used, hypochlorite is formed in the electrolytic cell, and the electrolyzed solution is then used for bleaching purposes. In a second type, no hypochlorite is formed in the cell; but the chlorine is treated with alkali outside the cell and before it is brought in contact with the substance to be bleached. In the third type the chlorine is led into the bleaching cell without being previously mixed with an alkaline solution.

The author gives a very careful discussion of all the more important patents and of very many of the minor ones. There is also a section on electrodes, addition of chemicals, such as chromates, methods of cooling, and general mechanical devices. A series of tables at the end of the book gives the different processes in chronological order, a comparative statement of yield, power and consumption of salt, together with an approximate statement of cost. This is one of the very good numbers of this series. *Wilder D. Bancroft*

**Die Elektrometallurgie der Alkalimetalle.** By H. Becker. (*Monographien über angewandte Elektrochemie, IX. Band.*) 16 × 24 cm; pp. iv + 135. Halle: Wilhelm Knapp, 1903. Price: paper, 6 marks. — There is an introductory chapter on the chemical processes for making the alkali metals and three pages on the electrolytic experiments of Davy and of Bunsen and Mathiessen. The electrolytic processes for the extraction of sodium are treated under the sub-heads: electrolysis of sodium chloride; electrolysis of caustic soda; electrolysis of mixtures of sodium hydroxide and sodium carbonate; electrolysis of sodium nitrate (Darling); preparation of sodium alloys. Under sodium alloys are included the Castner and the Acker processes for making caustic soda. Two pages are devoted to potassium and seven to lithium. There are a few pages on the electrothermal processes of Becker and of Cowles and a chapter on laboratory apparatus, including a discussion of the work of Fischer.

*Wilder D. Bancroft*

**Die elektrolytische Raffination des Kupfers.** By Titus Ulke. (*Monographien über angewandte Elektrochemie, X. Band.*) *Ins Deutsche übertragen von Viktor Engelhardt.* 16 × 24 cm; pp. x + 152. Halle: Wilhelm Knapp, 1904. Price: paper, 8 marks. — This is a translation of the author's book "Modern Electrolytic Copper Refining". The original has already been reviewed (7, 539).

*Wilder D. Bancroft*

**Karl Heumann's Anleitung zum Experimentieren bei Vorlesungen über anorganische Chemie.** By O. Kühling. *Dritte Auflage.* 15 × 23 cm; pp. xxxix + 818. Braunschweig: Friedrich Vieweg und Sohn, 1904. Price: paper, 19; bound, 20 marks. — The first edition of Heumann's well-known work appeared in 1876; this second in 1893, only a short time before the death

of its author; the second edition has recently been exhausted. In view of the development of experimental chemistry in several new directions during the last ten years, it was most desirable that a work like this, which one may well call a classic, should be subjected to a thorough revision before being again reprinted. One need only instance experiments at very high temperatures, — the electric furnace; the Goldschmidt process; and at very low temperatures, — liquid air; the use of the stereopticon for demonstrations; and the many recent lecture experiments in electrochemistry, to show the change in lecture room demonstration in recent years. Such a task of revision, then, has been undertaken by Prof. Kühling, who must be given the credit of having performed it with signal success. He has been both wise and fortunate in securing the co-operation of some of the most brilliant lecturers among the Germans; thus, he acknowledges his indebtedness to Erdmann, Emil Fischer, Landolt, Marckwald, and others; and many of the single experiments are indicated as due to one or other of these. And where personal assistance has not been obtained, experiments have been culled from many published sources.

All in all, we have here a unique collection; Heumann's book has for years been one of the indispensable adjuncts to the lecture preparation room; and in its present form it is if possible still more indispensable than it was.

While many of the experiments call for a somewhat elaborate equipment, such as is not found outside of the larger laboratories, there are also a great many that will be of value to those whose means are more restricted. It is one of the advantages of the present edition that it not only includes the description of many new experiments, but gives as well a discussion of the apparatus which is pre-supposed for them, — liquid air plant, storage battery equipment, stereopticon, etc., as well as a general plan of arrangement of lecture room and adjoining rooms.

The book is so very rich in material and suggestion, that it would lead us too far to go into a detailed consideration of even a part of it. The whole volume is commended to the attention of all of that "relatively small, but select, circle of readers" to whom it is intended to appeal. It is easily first among books of its kind, and in its new form it is a veritable mine of information and suggestion. No one who has to lecture on chemistry should be without it.

A. P. Saunders

**Kalender für Elektrochemiker sowie technische Chemiker und Physiker, für das Jahr 1904. VIII. Jahrgang. Mit einer Beilage. By A. Neuburger. 11 × 16 cm; pp. xxxiii + 596. Berlin: M. Krayn. Price: bound, 4 marks.** — This reference book has now stood the test for eight successive years and has deserved its success. The special novelties this year are the data for the electrical production of steel and accounts of the Edison and Jungner accumulators. Under electrolytic analysis is still to be found Vortmann's separation of cobalt from nickel, p. 451, although Vortmann never gave any details or any figures. Experiments made in the reviewer's laboratory lead him to doubt the possibility of a quantitative separation in a solution containing iodides.

It would be a convenience if that part of the table of contents which refers to the "*Beilage*" should be bound with it as well as with the main volume.

Wilder D. Bancroft

**Über den Anfangsunterricht in der Chemie.** By Julius Wagner. 15 X 23 cm; pp. 37. Leipzig: Johann Ambrosius Barth, 1903. Price: paper, 1.20 marks. — This address offers an intelligent, if not very suggestive discussion of the problems of secondary education in chemistry, for the conditions prevailing in Germany. It is worth the attention of those interested in the problem of the arrangement of elementary courses in chemistry. A. P. Saunders

**La Télégraphie sans Fils.** By André Broca. (*Actualités scientifiques.*) Deuxième Édition. 12 X 18 cm; pp. x + 234. Paris: Gauthier-Villars, 1904. Price. paper, 4 francs. — Broca's admirable popular account of the theory of the propagation of electric waves has been brought to date in a revised edition. There is nothing to be added to our appreciative review of the first edition (4, 542), beyond the statements that the revision has not altered the character of the book, and that the exposition has been extended by the addition of a chapter on syntony and currents of high frequency. J. E. Trevor

**Essais des Combustibles.** By D. Sidersky. (*Encyclopédie scientifique des Aide-Mémoire.*) 11 X 19 cm; pp. 185. Paris: Gauthier-Villars. Price: paper, 2.5; boards, 3 francs. — The first half of the volume deals with the methods of analysis of fuels and the other half with the calorimetric determinations. Among the industrial calorimeters are those of Mahler, Parr, Hartley and Junkers, and Darling. Wilder D. Bancroft

**Luftelektrizität und Sonnenstrahlung.** By H. Rudolph. 16 X 23 cm; pp. 24. Leipzig: Johann Ambrosius Barth, 1903. Price: paper, 1 mark. — This is a discussion of the state of electrification in the upper regions of the atmosphere. The reviewer confesses to an inability to follow the author's argument; but was somewhat consoled by the last paragraph, which implies that others have failed to be convinced by the author's eloquence. Wilder D. Bancroft

## REVIEWS

*The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry.*

### General

**On the determination of specific heats, especially at low temperatures.** *H. E. Schmitz. Proc. Roy. Soc. 72, 177 (1903).* — The author has determined the mean specific heat between  $-182^{\circ}$  and ordinary temperature for copper, thallium, lead, aluminum, cast iron, nickel, cobalt, zinc, silver, and tin. In each case the specific heat is lower than that at ordinary temperatures, the atomic heats for the mean temperature of  $-85^{\circ}$  coming out Cu 5.08, Tl 6.12, Pb 6.06, Al 4.66, Mi 4.93, Co 4.96, Zn 5.47, Ag 5.53, and Sn 5.91. *W. D. B.*

**On the temperature of flames.** *C. Fery. Comptes rendus, 137, 909 (1903).* — The author adds a sodium salt to the flame to be studied and determines the temperature at which the spectrum from a standardized incandescent lamp reverses the D lines. The temperature of a Bunsen burner at full blast is  $1871^{\circ}$ ; of an acetylene burner  $2548^{\circ}$ ; of hydrogen in air  $1900^{\circ}$ ; of the oxyhydrogen blowpipe  $2420^{\circ}$ . The temperatures given are mean values and are believed to be accurate to  $\pm 10^{\circ}$ . *W. D. B.*

**Calculation of the heats of combustion of the organic acids, their anhydrides and esters.** *P. Lemoult. Comptes rendus, 137, 656 (1903).* — For the monobasic acids the author writes  $Q = 157n - 106$  and for the dibasic acids  $Q = 157n - 212$ , where  $n$  is the number of carbons in the formula. For the esters the formula is  $Q = 157n - 90$ . *W. D. B.*

**A new method of calculating heats of combustion.** *P. Lemoult. Comptes rendus, 137, 979 (1903).* — The author's results can be summed up for non-cyclic compounds in the formula

$$Q = 157n + A_1.$$

Suitable changes have been made for cyclic compounds.

*W. D. B.*

### One-Component Systems

**Some physical properties of nickel carbonyl.** *J. Dewar and H. O. Jones. Proc. Roy. Soc. 71, 427 (1903).* — By using atmospheres of inert gases it is possible to make vapor density determinations of nickel carbonyl even up to  $216^{\circ}$ . It was found that the rate at which the liquid evaporated had an effect on the extent of the dissociation. In an atmosphere of carbon monoxide at  $100^{\circ}$  a determination was obtained, showing less than one percent dissociation. The critical temperature is probably about  $200^{\circ}$ , the value of  $195^{\circ}$  actually found being probably lowered by the presence of carbon monoxide. The critical pressure is probably about thirty atmospheres. The vapor pressure curve has been



determined from  $-10^{\circ}$  to the boiling-point at  $43.2^{\circ}$ . The latent heat of vaporization is 38.1 calories per gram and the Trouton constant is 20.6.

W. D. B.

The vapor pressures of liquid oxygen on the scale of the constant-volume oxygen thermometer filled at different initial pressures. *M. W. Travers and C. J. Fox. Proc. Roy. Soc. 72, 386 (1903).* — The mean values of the difference of the temperatures corresponding to the vapor pressures of liquid oxygen on the scales of the oxygen and the helium thermometers, when plotted against the initial pressures at which the oxygen thermometer was filled are found to be nearly on a straight line. The differences are  $1.18^{\circ}$  at 731 mm and  $0.77^{\circ}$  at 336 mm if we take the experimental values. If we take the smooth values the differences are  $0.72^{\circ}$  at 336 mm and  $0.4^{\circ}$  by extrapolation to zero pressure.

W. D. B.

On the compressibilities of oxygen, hydrogen, nitrogen and carbonic oxide between one atmosphere and half an atmosphere of pressure, and on the atomic weights of the elements concerned. *Lord Rayleigh. Proc. Roy. Soc. 73, 153 (1904).* — The ratio of  $pv$  for  $p = 0.5$  atm to  $pv$  for  $p = 1.0$  atm is found to be 1.00040 for oxygen, 0.99976 for hydrogen, 1.00017 for hydrogen, and 1.00028 for carbon monoxide. The author points out that, if Avogadro's law is applicable at low pressures, the atomic weight of nitrogen must be less than 14.01 instead of the 14.05 found by Stas. The ratios of the vapor densities of hydrogen and carbon monoxide to the vapor density of oxygen are so close to the ratios of the atomic weights that it evidently seems very improbable to the author that there should be any such discrepancy with nitrogen as is implied in Stas's value.

W. D. B.

On the measurement of the pressure coefficient of oxygen at constant volume and different initial pressures. *W. Makower and H. R. Noble. Proc. Roy. Soc. 72, 379 (1903).* — By extrapolation, the value of the pressure coefficient for oxygen at zero initial pressure is found to lie between 0.003664 and 0.003665. This is higher than the value of 0.0036625 found by Travers and Jaquero for hydrogen by the same method. Using the Callendar method and the pressure coefficient just found, the difference between  $\theta$ , the temperature on the thermodynamic scale, and  $T$ , the temperature by the gas thermometer, is found to be  $0.913^{\circ}$ . This makes  $\theta_0 = 273.09$ .

W. D. B.

The density of chlorine. *H. Moissan and Binet du Jassoneix. Comptes rendus, 137, 1198 (1903).* — The determination of the density of chlorine by the Dumas method gave values at first which varied between 2.424 and 2.506. The chief sources of error were: air in the bulb; moisture; and the solubility of other gases in liquid chlorine. When these errors were eliminated as completely as possible, the density of chlorine at  $0^{\circ}$  was found to be 2.490.

W. D. B.

The state of vaporized carbon. *M. Berthelot. Comptes rendus, 137, 589 (1903).* — A study of the filaments of incandescent lamps and of the black deposit on the inside of old lamps, shows that both are amorphous carbon and that the carbon does not precipitate from the vapor as graphite. It is main-

tained that carbon is not always the same, as the degree of polymerization varies with the temperature. *W. D. B.*

Some remarks on molecular transformation. *J. D. van der Waals. Arch. néerl. (2) 8, 104 (1903).* — In the case of acetic acid and nitrogen peroxide, the molecular complexity decreases with rising temperature. With acetaldehyde and paraldehyde, the effect of pressure is so great that the percentage of paraldehyde in the vapor appears to pass through a minimum with rising temperature. The author discusses the way in which this appears in the gas equation for two components in reversible equilibrium. In the case under consideration, the pressures are so high that it is unsafe to deduce the composition of the vapor from the density. *W. D. B.*

Equilibria in the system acetaldehyde and paraldehyde with and without molecular changes. *H. W. Bakhuis Roozeboom. Arch. néerl. (2) 8, 97 (1903).* — This is essentially an abstract of Hollemann's paper (7, 476). *W. D. B.*

#### Two-Component Systems

A representation in space of the fields for the components of a binary system and their complexes when only the components occur as solids. *H. W. Bakhuis Roozeboom. Arch. néerl. (2) 8, 92 (1903).* — A very complete discussion of the pressure-temperature-concentration diagram for the simplest type of two-component systems, in which there is only one liquid phase and the two components form no solid compounds and no solid solutions. Two photographs of a solid model help to make the text clearer. *W. D. B.*

On the nature of the inactive diformalic derivative of racemic acid. *W. E. Ringer. Recueil Trav. Pays-Bas, 21, 374 (1902).* — The freezing-point curve for the dextro-rotary and the inactive diformalic derivatives of tartaric acid shows that the inactive form is a compound and not a mixture of the two optically active forms. *W. D. B.*

The properties of the aluminum-tin alloys. *W. C. Anderson and G. Lean. Proc. Roy. Soc. 72, 277 (1903).* — The authors give data for the liquidus and for the solidus curve for aluminum and tin. The latter curve is certainly wrong and the flat in the freezing-point curve has since been shown not to exist (8, 233). With this pair of metals it is practically impossible to obtain results which mean anything unless the melt is stirred while cooling. *W. D. B.*

On certain properties of the alloys of the gold-silver series. *W. C. Roberts-Austen and T. K. Rose. Proc. Roy. Soc. 71, 161 (1903).* — The freezing-point curve for gold and silver has been re-determined. The two metals form a continuous series of solid solutions and consequently any mixture must be homogeneous after annealing. It is shown that this is the case for the alloy containing 91.66 percent gold. The English law requires that the trial plates for testing the standard of the coinage shall contain 916.6 parts of gold and 83.3 parts of some other metal, the nature of this latter not being specified. Since 1873 the other metal has been copper, but a change was made in 1902 to silver on account of the importance of obtaining homogeneous trial-plates. *W. D. B.*

**Constant-standard silver trial-plates.** *E. Matthey. Proc. Roy. Soc.* 73, 124 (1904). — By using a thin cold mould and filling it from the bottom, the author casts standard silver trial-plates weighing as much as 8 to 10 kilograms, which are practically homogeneous. The author states that this method of casting contradicts the belief "that a uniformity of standard was best obtained by slow and uniform cooling." He overlooks the fact that what is best for a gold-silver alloy is not the best for a silver-copper alloy. The first pair of metals forms a continuous series of solid solutions; the second pair forms two series of solid solutions with very limited solubility. This must be kept in mind in considering the conditions for getting a homogeneous plate. *W. D. B.*

**Dissociation of the alkali carbonates.** *P. Lebeau. Comptes rendus*, 137, 1255 (1903). — Determinations were made of the dissociation pressures of sodium, potassium, rubidium and caesium carbonates at temperatures between 700° and 1200°. Potassium carbonate is the most stable, the order being potassium, sodium, rubidium and caesium. *W. D. B.*

**The fusibility of mixtures of sulphur and bismuth.** *H. Pélabon. Comptes rendus*, 137, 648 (1903). — The bismuth used by the author is said in one paragraph to have melted at 255° and in another at 260°. Addition of sulphur is said to have caused a rise of freezing-point. At 435° and a composition of sixteen atoms of bismuth to one of sulphur there is a quadruple point. No attempt is made to determine the phases at this point. There is another quadruple point at 685° and a composition of one of bismuth to one of sulphur. From this the author deduces the existence of the compound BiS, apparently believing that the solution at a quadruple point always has the composition of a compound. It is more than probable that the variable melting-point of bismuth masked a eutectic. Altogether this is an inexcusably inaccurate and careless piece of work. *W. D. B.*

**On the fusibility of the mixtures of bismuth and silver sulphides and of the sulphides of bismuth and antimony.** *H. Pélabon. Comptes rendus*, 137, 920 (1903). — This is another bit of inaccurate work. The freezing-point curve for bismuth sulphide and silver sulphide is said to show two eutectics, an angular maximum and a quadruple point which is not a maximum. The angular maximum represents experimental error; the assumption that the co-ordinates of the quadruple point give the composition of the solid phase is a theoretical error.

The freezing-point curve for bismuth sulphide and antimony sulphide is said to consist of three parts with neither maximum nor minimum. There is nothing in the experiments to show whether these breaks are real or imaginary. In any case they cannot have the significance attributed to them by the author. *W. D. B.*

**On mixtures of antimony and antimony trisulphide.** *H. Pélabon. Comptes rendus*, 138, 277 (1904). — Antimony sulphide and antimony form two liquid layers with a quadruple point at 615°. The author takes the melting-point of pure antimony as 632° and that of the sulphide as 555°. The eutectic temperature is 515°. *W. D. B.*

**Crystallization and dissociation in solid solution.** *C. A. Lobry de Bruyn*

and C. L. Jungius. *Recueil Trav. Pays-Bas*, 22, 298 (1903). — Under the influence of light, solid *o*-nitrobenzaldehyde changes into *o*-nitrosobenzoic acid. Up to a certain extent the acid remains dissolved in the aldehyde, giving a green color. When the concentration of the acid exceeds 2.6 molecular percents, the excess crystallizes as a white solid. *W. D. B.*

**Critical phenomena with partially miscible liquids.** *J. D. van der Waals. Arch. néerl.* (2) 8, 109 (1903). — Mixtures of ethane and ethyl alcohol give two separated curves of folding. The author had previously joined these two theoretically by means of a continuous curve. The experiments of Kuenen lead him now to consider these two lines as joined by a third, making sharp angles with the other two. The matter is discussed at length and it is shown that this new point of view excludes the possibility of a maximum temperature. *W. D. B.*

**Experimental investigations on distillation.** *E. Charabot and J. Rocherolles. Comptes rendus*, 138, 497 (1904). — The authors consider the case in which the vapor of one liquid is bubbled through a second non-miscible liquid kept at a temperature higher than the boiling-points of the mixed liquids. Under these circumstances, the first liquid cannot condense and there will be a definite relation between the composition of the distillate and the vapor pressures of the two liquids provided equilibrium is reached. In any actual case it is difficult to reach equilibrium, but the experiments of the authors do not show this. *W. D. B.*

**The extraction of oxygen by partial liquefaction of air and a reverse flow.** *G. Claude. Comptes rendus*, 137, 783 (1903). — The author condenses a part of the air under moderate pressure and makes the liquid flow in the opposite direction to the condensing gas. In this way he gets a liquid containing 55 percent oxygen and a gas containing 97 percent nitrogen without having to liquefy all the air. This result was made possible by a study of the phase rule. *W. D. B.*

**The evaporation of water in a current of air.** *E. P. Perman. Proc. Roy. Soc.* 72, 72 (1903). — The author draws the following conclusions:

1. When air is aspirated through water, it becomes saturated with aqueous vapor with great rapidity.
2. In the saturated air so obtained, the pressure of the aqueous vapor is the same as the vapor pressure of water when no other gas is present.
3. The density of the aqueous vapor in the mixture is normal.
4. The density of saturated aqueous vapor (without admixture) is probably only very slightly (if at all) above normal at temperatures up to 90°.

*W. D. B.*

**Some addition products of different acids.** *S. Hoogewerff and W. A. van Dorp. Recueil Trav. Pays-Bas*, 21, 349 (1902). — The authors give a list of thirty-four organic substances, which have been obtained with sulphuric acid of crystallization. In each case the compound is decomposed by the action of solvents. The authors, however, discuss the question whether one is to assume the presence of quadrivalent oxygen in these substances or not. *W. D. B.*

**The density and the expansion with heat of magnesium chloride solutions.** *G. J. W. Bremer. Recueil Trav. Pays-Bas, 21, 59 (1902).*—The author has determined the densities of solutions containing from six to twenty grams of magnesium chloride per hundred cubic centimeters of solution at temperatures from 15° to 100°. With the more dilute solutions, density determinations were made down to -6°. At low temperatures the expansion per degree is greatest for the most concentrated solutions, but the reverse is true for the higher temperatures. Starting with the same volumes at 0°, the solutions have the same volumes at about 56° + 3.

*W. D. B.*

#### *Multi-Component Systems*

**The sulphates of potassium.** *W. Stortenbeker. Recueil Trav. Pays-Bas, 21, 399 (1902).*—Solubility curves have been determined for some mixtures of potassium sulphate, sulphuric acid and water. The stable solid phases were  $K_2SO_4$ ,  $K_2SO_4 \cdot KHSO_4$  and  $KHSO_4$ . As instable solid phases we have  $K_2SO_4 \cdot 3KHSO_4$  and  $K_2SO_4 \cdot 6KHSO_4$ .

*W. D. B.*

**The hydrates of nickel sulphate and methyl alcohol.** *C. A. Lobry de Bruyn. Recueil Trav. Pays-Bas, 22, 407 (1903).*—The author has determined the solubility of various hydrates of nickel sulphate in methyl alcohol solutions of different strengths. The values are only approximate ones because these hydrates are not stable. The stable solid phase has the composition  $NiSO_4 \cdot 3CH_3OH \cdot 3H_2O$ .

*W. D. B.*

**On the state in which the hydrated nickel sulphates occur in methyl alcohol solutions.** *C. A. Lobry de Bruyn and C. L. Jungius. Recueil Trav. Pays-Bas, 22, 421 (1903).*—Boiling-point measurements appear to show that  $NiSO_4 \cdot 7H_2O$  loses  $6H_2O$  when dissolving in methyl alcohol. If the sulphate retains one of water in methyl alcohol, the authors feel certain that it must retain at least as much in aqueous solutions.

*W. D. B.*

**The application of physical chemistry to the study of toxins and antitoxines.** *S. Arrhenius and T. Madsen. Zeit. phys. Chem. 44, 7 (1903).*—This is an investigation of the effect of antitoxines (salts, proteids, normal serum, antitetanolyisin, etc.) on the power of toxins (ammonia, alkalies, tetanolyisin) to produce hæmolysis of blood corpuscles, and an attempt to explain the results on the basis of the mass law. The method of investigation consisted in allowing the toxic solution to react at 37° with a suspension of the blood corpuscles, and, after removal of the undestroyed corpuscles, estimating the extent of hæmolysis colorimetrically. The results and their interpretation are hardly definite enough to give in abstract, but the following striking cases may be mentioned. The decrease in the toxicity of tetanolyisin caused by increasing quantities of antitetanolyisin is exactly proportional to the free toxin calculated from the mass law equation :

$$\text{free toxin} \times \text{free antitoxine} = K(\text{toxin-antitoxine-compound})^2.$$

An analogous case in which ammonia was the toxin and boric acid the antitoxine was investigated and the results were found to be in accord with the mass law.

*F. B. K.*

**Ternary systems.** *J. D. van der Waals. Arch. néerl. (2) 7, 343 (1902).*— This is an elaborate study of the  $\zeta$  function as applied to ternary systems.

*W. D. B.*

**On the conditions for the existence of a minimum critical temperature in a ternary system.** *J. D. van der Waals. Arch. néerl. (2) 8, 69 (1903).*— The general conclusion reached is that the conditions for a minimum critical temperature in a ternary system are given if we know the behavior of the three binary systems.

*W. D. B.*

**Vapor pressures in the system: water, acetone and phenol.** *F. A. H. Schreinemakers. Arch. néerl. (2) 8, 1 (1903).*— Reviewed (7, 229) from Zeit. phys. Chem. 39, 485; 40, 440; 41, 331 (1902).

**Vapor pressures of ternary mixtures.** *F. A. H. Schreinemakers. Arch. néerl. (2) 8, 99 (1902).*— Reviewed (7, 228) from Zeit. phys. Chem. 36, 257, 412, 711; 37, 129; 38, 227 (1901).

**Some remarks on the vapor pressures of ternary mixtures.** *F. A. H. Schreinemakers. Arch. néerl. (2) 8, 395 (1903).*— Reviewed (7, 545) from Zeit. phys. Chem. 43, 671 (1903).

**Direct preparation of cyclohexanol and of cyclohexanone from phenol.** *F. Sabatier and J. B. Senderens. Comptes rendus, 137, 1025 (1903).*— When a mixture of phenol vapor and hydrogen is passed over nickel powder at 140°–150° there is formed cyclohexanol,  $C_6H_{11}OH$ . By passing the same mixture first over nickel at 215°–250° and then over copper at 330°, there is obtained cyclohexanone,  $C_6H_{10}O$ .

*W. D. B.*

**Direct hydrogenization of aniline.** *P. Sabatier and J. B. Senderens. Comptes rendus, 138, 457 (1904).*— When hydrogen and aniline are passed over pulverulent nickel heated to 190°, there is a condensation, and also an evolution of ammonia. The product consists chiefly of  $C_6H_{11}NH_2$  boiling at 134°,  $(C_6H_{11})_2NH$  boiling at 250°, and  $C_6H_5NHC_6H_{11}$  boiling at 275°. The last two substances are new.

*W. D. B.*

**Direct reduction of aromatic halogen compounds by pulverulent nickel and hydrogen.** *P. Sabatier and A. Mailhe. Comptes rendus, 138, 245 (1904).*— When hydrogen and chlorobenzene are passed over pulverulent nickel at 270°, nickel chloride and benzene are formed, with traces of diphenyl. At the same temperature 30 percent of *m*-dichlorobenzene was converted into benzene; 60 percent into chlorobenzene, while about 10 percent was unchanged. At 200° *o*- and *m*-chloranilines are reduced to aniline. Brombenzene is also readily reduced, but the iodine compounds are more refractory, apparently because hydriodic acid reacts less readily with nickel.

*W. D. B.*

**Synthesis of hydrogenized aromatic alcohols.** *L. Brunel. Comptes rendus, 137, 1269 (1903).*— The method was that of Sabatier and Senderens. By passing hydrogen and phenol over nickel at 170°–175°, a practically quantitative yield of cyclohexanol,  $C_6H_{11}OH$ , was obtained. In this experiment about 250 cc of hydrogen passed through the tube per minute and about 12 g of phenol per hour.

With thymol and hydrogen at 180°–185° hexahydrothymol,  $C_{10}H_{18}OH$ , is obtained, while hexahydrocarvacrol can be prepared by passing carvacrol and hydrogen over nickel heated to 195°–200°.

W. D. B.

**Alcoholic fermentation.** J. H. Abersson. *Recueil Trav. Pays-Bas*, 22, 78 (1903). — The alcoholic fermentation of sugar is a monomolecular reaction modified by action due to the glucose and alcohol. The temperature coefficient is normal. The reaction does not run to an end, and adding the reaction products causes equilibrium to be reached sooner. On the other hand it was not possible to effect a reversal of the reaction.

W. D. B.

**A rigorous separation in the rare earth series.** G. Urbain and H. Lacombe. *Comptes rendus*, 137, 792 (1903). — The authors make the erroneous statement that it is not possible to separate by fractional crystallization two salts which are not isomorphous. [This is true only in case one insists on crystallizing always at the same temperature (2, 43)]. With isomorphous mixtures fractional separation can be effected at constant temperature, but the process is a slow one. By adding a third component isomorphous with the two rare earth elements, having an intermediate solubility and easily separable by chemical means, the separation can be made more quickly. The authors have added to the double magnesium nitrates of the earths rich in samarium a large amount of the double nitrate of magnesium and bismuth. The neodymium came out in the first fractions and then the samarium, while the last fractions were almost exclusively bismuth. When the double nitrate of magnesium and bismuth is added to the double magnesium nitrates of the rare earths rich in gadolinium, the first fractions contained the bismuth and the last the rare earths. From this the authors conclude that it would be easy to separate samarium from gadolinium by means of bismuth, but they did not actually do it.

W. D. B.

**Action of quick-lime on carbon at the fusing temperature of platinum.** H. Moissan. *Comptes rendus*, 138, 243 (1904). — Quick-lime and sugar carbon were heated in a quartz tube to a temperature at which platinum fuses. No reaction took place and a piece of calcium carbide does not soften at that temperature. It was noticed that silica sublimes slowly from the quartz tubes even at 1200°, forming needles of a calcium silicate.

W. D. B.

**Chemical nature of colloidal solutions.** J. Duclaux. *Comptes rendus*, 138, 144 (1904). — It is pointed out that the colloidal substance obtained by mixing potassium ferrocyanide and copper sulphate solutions always contains potassium, the amount decreasing with increasing excess of copper sulphate solution. From this and other experiments, the author draws the very proper conclusion that the composition of the colloid is fixed only when that of the solution is fixed. As he does not consider the possibility of the colloid being a second solution phase, he is very much puzzled by the results.

W. D. B.

**An attempt to estimate the relative amounts of krypton and of xenon in atmospheric air.** W. Ramsay. *Proc. Roy. Soc.* 71, 421 (1903). — Reviewed (7, 597) from *Zeit. phys. Chem.* 44, 74 (1903).

**New preparation of argon.** H. Moissan and A. Rigaut. *Comptes ren-*

*du*, 137, 773 (1903). — Metallic calcium combines with nitrogen at a red heat, forming  $\text{Ca}_3\text{N}_2$ , and with hydrogen at the same temperature, forming  $\text{CaH}_2$ . This property has been made use of in the precipitation of argon. There are four steps in the process. In the first oxygen is removed by copper; in the second some of the nitrogen is removed by magnesium and lime; in the third the bulk of the nitrogen is taken out also by magnesium and lime; in the fourth step the last five percent of nitrogen is removed with metallic calcium. After the apparatus is set up and tested, two people can make a liter of argon in twelve hours.

W. D. B.

**Examination of the gases occluded or set free by radium bromide.** *J. Dewar and P. Curie. Comptes rendus*, 138, 190 (1904). — A small sample of radium bromide was placed in a vacuum for three months. Some gas was given off which appeared to be hydrogen, and which probably came from traces of moisture. The radium bromide was then placed in a quartz tube, a vacuum established, and the tube heated until the radium bromide fused. More gas was given off and was condensed in another tube by means of liquid air. The quartz tube containing the radium was then sealed in the oxyhydrogen blow-pipe. The condensed gases were self-luminous and showed nitrogen bands. When the tube containing the radium bromide was excited by an induction coil, the complete spectrum of helium was obtained.

W. D. B.

**Action of oxygen and hydrochloric acid on some metals.** *C. Matignon. Comptes rendus*, 137, 1051 (1903). — In presence of oxygen, hydrochloric acid attacks the platinum metals at temperatures below that at which hydrochloric acid is oxidized. Palladium reacts cold; ruthenium readily at  $125^\circ$ ; iridium, rhodium and osmium at  $150^\circ$ .

W. D. B.

**New method of determining critical points of irons and steels.** *O. Boudouard. Comptes rendus*, 137, 1054 (1903). — A bar of metal, 10 cm in length, is taken and the thermo-electric force between the two ends is measured as a function of the temperature. This is said to give a very satisfactory method of determining transition points.

W. D. B.

**Allotropic changes of nickel steels.** *O. Boudouard. Comptes rendus*, 138, 370 (1904). — The author has determined the so-called transition points for nickel steels containing 0.12 and 0.8 percents carbon and percentages of nickel varying from two to thirty. The results are very irregular, so much so as to make one wonder what their real accuracy is. It may be desirable to determine apparent temperatures of change; but it certainly would be well to determine equilibrium temperatures also.

W. D. B.

**The styles of deformation and rupture of irons and soft steels.** *F. Osmond, C. Frémont and G. Carlaud. Comptes rendus*, 137, 851 (1903). — The authors consider the polyhedral grains usually found in cast or wrought iron as cellular in nature, and they therefore speak of iron as occurring in the amorphous, cellular and crystalline states. Cellular iron is supposed to be very plastic, while crystalline iron is brittle. This duality is believed to explain many of the peculiarities of iron and steel.

W. D. B.

**The constitution and properties of vanadium steels.** *L. Guillet. Comptes*



*rendus*, 138, 367 (1904). — With a steel containing 0.2 percent carbon, vanadium could not be detected until its concentration exceeded 0.7 percent. With a steel containing 0.8 percent carbon, vanadium could be detected microscopically when its concentration exceeded 0.5 percent. It is not known in what form the excess of vanadium separates. Vanadium steels are so brittle that they appear to be worthless except possibly for tools.  
W. D. B.

The constitution and properties of silicon steel. *L. Guillet. Comptes rendus*, 137, 1052 (1903). — With up to five percent silicon in iron, the silicon cannot be detected microscopically. With five to seven percent silicon part of the carbon is present as graphite, while the carbon is all changed to graphite when the silicon exceeds seven percent. The author hazards no guess at the form in which the silicon appears after its concentration exceeds five percent. A steel containing over five to seven percent of silicon cannot be worked.  
W. D. B.

#### Osmotic Pressure and Diffusion

On osmotic pressure. *A. Smits. Recueil Trav. Pays-Bas*, 22, 153 (1903). — If we have two solutions of benzene and ether separated by a membrane permeable to ether only, ether will pass from the place of higher concentration to the place of lower concentration. If the solutions are separated by a membrane permeable only to benzene, benzene will pass through the membrane in the opposite direction. From this the author deduces the conclusion that there is no theoretical difference between the solvent and the solute. The author makes the common mistake of trying to deduce quantitative conclusions from qualitative experiments. The question is whether there is a difference in the quantitative relations. Superficially there is. The change of the vapor pressure of the solvent is dependent chiefly on the concentration of the solute and is independent of the nature of the solute for limiting cases. The vapor pressure of the solute varies much more with the nature of the solvent than with its molecular concentration. So far as the facts are concerned, there is a fundamental difference between solvent and solute. This difference can be made to disappear by saying that in one case we are dealing with concentrated solutions and that any discrepancy is possible in a concentrated solution. This may, of course, be true; but it has never been proved.  
W. D. B.

On osmosis. *A. Guillemin. Comptes rendus*, 138, 38 (1904). — It is repugnant to the author to consider sugar dissolved in water as behaving like a gas. He prefers to assume that osmotic pressure is due to water vapor dissolved in liquid water.  
W. D. B.

Relation between diffusion and viscosity. *J. Thoverl. Comptes rendus*, 138, 481 (1904). — Experiments on the rate of diffusion of phenol in twelve solvents have shown that the diffusion constant of phenol multiplied by the relative viscosity of the solvent is very nearly a constant for the whole twelve.  
W. D. B.

On the measurement of the diffusion of salts in solution. *J. C. Graham. Proc. Roy. Soc.* 72, 212 (1903). — A description of an apparatus for 'floating' pure water on a denser salt solution. Tables are also given for calculating the

diffusion coefficient. There are no actual data on the diffusion of any particular salt.

W. D. B.

#### Velocities

**The inversion of sugar.** *L. Lindel. Comptes rendus*, 138, 508 (1904). — The author has studied the rate of inversion of sugar in distilled water at 100°. Presence of copper, lead, tin or bismuth increases the rate of inversion very much, aluminum or antimony but slightly. Nickel, chromium, arsenic, gold, platinum, silver and mercury have practically no effect, while cobalt, iron, zinc, cadmium and magnesium retard the inversion. Alumina increases the rate much more than does aluminum.

W. D. B.

**Studies of dynamic isomerism, I.** *T. Lowry. Jour. Chem. Soc.* 83, 1314 (1903). — The rate of change of rotation of a 5 percent glucose solution was measured in the presence of hydrochloric acid, potash and potassium chloride of various concentrations. From the fact that the mutarotation of aqueous solutions of glucose was not checked by the addition of small quantities of acid, the author concludes that the process cannot be due to the presence of traces of alkali in the solution.

F. B. K.

**The rate of decomposition of diazo-compounds, II.** *J. C. Cain and F. Nicoll. Jour. Chem. Soc.* 83, 206 (1903). — This is an extension of the former investigation (7, 231) to the diazo-salts of the following amines:  $\alpha$ -naphthylamine and its monosulphonic acids ( $\text{NH}_2 : \text{SO}_3\text{H}$ , 2, 4, 5, and 8);  $\beta$ -naphthylamine and its monosulphonic acids ( $\text{NH}_2 : \text{SO}_3\text{H}$ , 6 and 7); and disulphonic acids ( $\text{NH}_2 : \text{SO}_3\text{H}$ , 3 : 6 and 6 : 8); 7-amino- $\alpha$ -naphthol-3-sulphonic acid, and 8-amino- $\alpha$ -naphthol-3 : 6-disulphonic acid. With soluble diazo-compounds good first order constants were obtained "up to the point" where the hydroxy product began to couple with the undecomposed diazo-salt to form azo-compounds. From this point on, the solutions became colored and the constants fell off rapidly. Though it is not likely that the diazo-salt and naphthol can exist side by side up to a certain point, as assumed by the authors, the decrease in the constant certainly becomes very rapid at a certain stage of the process. In the case of insoluble diazo-compounds the rate of decomposition was found to be constant. Most of the experiments were carried out at 60°. *F. B. K.*

**The rate of decomposition of diazo-compounds, III.** *J. C. Cain and F. Nicoll. Jour. Chem. Soc.* 83, 470 (1904). — Calculation of temperature coefficients of the velocity constants from Parts I and II of the investigation.

F. B. K.

**The conditions of decomposition of ammonium nitrite.** *V. H. Veley. Jour. Chem. Soc.* 83, 734 (1903). — The decomposition of ammonium nitrite is a monomolecular reaction both in the presence and absence of an accelerator. The reaction is impeded or stopped by ammonia, and oxides which liberate ammonia; also by amines, hydrazines and, to a lesser degree, by oximes. Amides of the paraffin series cause a temporary acceleration, while benzamide and urea have no influence. Benzoic sulphinide caused considerable acceleration. The experiments were carried out between 60° and 70°. *F. B. K.*

**The enzyme of blood which decomposes hydrogen peroxide, I.** *G. Sen-*

*ter. Zeit. phys. Chem.* **44**, 257 (1903). — The author has definitely established the fact that the enzyme of blood which causes the decomposition of hydrogen peroxide is neither the stromata nor the hæmoglobin, but can be separated from the latter by precipitation by 50 percent alcohol. The enzyme obtained by extracting the precipitate is called hæmase. It differs from hæmoglobin in not giving a blue color with a mixture of hydrogen peroxide and guajak. The decomposition of hydrogen peroxide by hæmase was followed quantitatively, and in the case of dilute solutions was found to accord very closely with the formula for monomolecular reactions. The effect of acids, sodium hydrate, salts and the enzyme poisons, aniline and hydrocyanic acid, was investigated. Most of the experiments were carried out at 0°, to avoid the oxidation of the enzyme by the peroxide, but the temperature coefficient between 0° and 10° was also determined. A good account is given of previous work done on the blood enzyme.  
F. B. K.

**The multirotation of milk sugar.** *C. S. Hudson. Zeit. phys. Chem.* **44**, 485 (1903). — Solutions of milk sugar hydrate and milk sugar lactone show multirotation, both finally giving the same value. The author shows that the phenomenon is due to the two solutions gradually approaching a common state of equilibrium between the two substances. The sum of the two velocity constants is determined by following the change of a solution of milk sugar hydrate, while a similar investigation of a solution in equilibrium with solid hydrate leads to a determination of the values of the individual constants.  
F. B. K.

**The catalytic racemisation of amygdalin.** *J. W. Walker. Jour. Chem. Soc.* **83**, 472 (1903). — From a polarimetric investigation of the racemisation of amygdalin, the author shows that it is probable that the process is a catalytic one induced by the presence of alkalies.  
F. B. K.

**The velocity of intramolecular change among the halogen acetanilides, II.** *J. J. Blanksma. Recueil Trav. Pays-Bas*, **22**, 290 (1903). — In the first paper (7, 232) it was shown that the change of acetyl chloranilide into *p*-chloracetanilide is a monomolecular reaction taking place in aqueous acetic acid or aqueous alcohol solutions with hydrochloric acid as a catalytic agent. It is now shown that the rate of change decreases as the amount of water present increases. With decreasing concentration of hydrochloric acid, the rate apparently tends toward zero as a limit. This involves a considerable extrapolation.  
W. D. B.

**The rate of reaction between bromine and ethyl alcohol, II.** *S. Bugarszky. Zeit. phys. Chem.* **42**, 543 (1902). — By carrying out the reaction at different temperatures and varying the initial concentrations of the bromine and hydrobromic acid, the author is able to calculate the temperature coefficient of the velocity constant of the monomolecular reaction and also that of the dissociation constant of the hydrogen tribromide. (Cf. 6, 154.) From the latter value he calculates the heat of dissociation and finds the number to agree well with the result of a direct determination. The author makes his article look extremely formidable by the unnecessary repetition of his integrated reaction formula at the top of each column of constants.  
F. B. K.

The chemical dynamics of the reaction between chlorine and benzene under the influence of different catalytic agents and of light. *A. Slator. Zeit. phys. Chem.* 45, 513; *Jour. Chem. Soc.* 83, 729 (1903).—Measurements were made of the effect of catalyzers on the formation of  $C_6H_5Cl$  and  $C_6H_6Cl_2$  from benzene and chlorine. In the presence of iodine chloride the rate was proportional to the concentration of the chlorine and of the benzene and to the square of the concentration of the catalyzer. The relative amount of the chlorine, which went to form the substitution product (about 70 percent) was independent of the concentrations. With stannic chloride and with ferric chloride the substitution product only was obtained, the rate being proportional to the concentrations of the chlorine and of the catalyzer. When a mixture of iodine chloride and stannic chloride was used the rate was found to be equal to the sum of the rates due to the individual catalyzers. Under the influence of light, addition of the chlorine took place with a velocity proportional to the first power of the benzene concentration. For diluting the benzene, carbon tetrachloride was employed. Temperature coefficients between  $15^\circ$  and  $20^\circ$  were determined. *F. B. K.*

The kinetics of carbon monoxide and oxygen mixtures. *H. Köhl. Zeit. phys. Chem.* 44, 385 (1903).—The combination of oxygen with carbon monoxide in the presence of varying concentrations of water vapor was followed by manometric measurements. The reaction was carried out in a porcelain vessel kept at  $575^\circ$  in a thermostat of molten lead. In some of the experiments carbon dioxide was also added. As is generally the case with gases, unaccountable disturbing influences made it impossible to collate the results by any consistent assumption as to the nature of the reaction. Among other things, the order in which the gases were introduced into the vessel, exercised a surprising effect on the rate. The experiments, however, seem to establish one important fact, namely, that the velocity is largely independent of the concentration of the oxygen. *F. B. K.*

Studies on the coupling of chemical processes, I. *N. Schilow. Zeit. phys. Chem.* 42, 641 (1902).—This article contains the experimental results of an investigation of a number of cases of induced reaction, the theoretical discussion of which is reserved for a future communication (8, 228). The following reactions were studied: Fehling's solution + oxidizing agents, ammonia + hypochlorite in the presence of oxidizing agents, oxy-acids + chromic acid + arsenious acid, oxy-acids + permanganate + reducing agents, oxy-acids + chromic acid + sulphurous acid, bromic acid + arsenious acid + reducing agents (sulphurous acid, formaldehyde and ferro-ion), bromic acid + chromic acid + arsenious acid, bromic acid + arsenious acid + hydrobromic acid. The latter reaction affords an example of "self-induction", the process being interpreted as follows. It is assumed that the primary reaction is



that  $HBrO_3 + HBrO + As_2O_3$  react instantaneously and that direct reaction between bromic acid and arsenious acid does not take place. The reaction formula set up on this assumption gives an excellent constant with varying con-

centrations of hydrobromic acid and of arsenious acid, and the inflection point in the reaction curve occurs at the point calculated from the formula.

F. B. K.

On negative catalyzers in a homogeneous system. *A. Titoff. Zeit. phys. Chem.* 45, 641 (1903). — This is a continuation and amplification of Bigelow's research on the oxidation of sodium sulphite by free oxygen (3, 183). Instead of bubbling oxygen through the liquid, the author uses an aqueous solution of the gas, and thus avoids the cumulative effect of impurities in the oxygen. He finds the same difficulties experienced by Bigelow in obtaining concordant results, owing to the presence of traces of impurity in the water, but he establishes the fact that the rate decreases with the purification of the water used. Copper sulphate proved to be an extraordinarily powerful catalyzer, the rate of oxidation being appreciably increased by the presence of  $6 \times 10^{-8}$  grams copper per liter. The action of the so-called negative catalyzers appeared to be due to the neutralization of traces of positive catalyzers. The chlorides of tin were found to be retarding agents of even greater power than mannite. The author begins the summary of his results with the statement that "for the first time, a case of definite negative catalysis in a homogeneous medium has been discovered and measured". This, though literally true, might in view of Bigelow's research, have been with advantage less pretentiously expressed.

F. B. K.

Influences accelerating or retarding the action of manganese as metallic ferment. *A. Trillat. Comptes rendus*, 137, 922 (1903). — The absorption of oxygen by an alkaline solution of hydroquinone, pyrogallol, tannin, etc., is accelerated by the presence of traces of a manganese salt, though further additions of manganese may act unfavorably. Increasing the concentration of alkali increases the rate of absorption. Quartz and other substances have a disturbing effect. No reference is made to the work that has been done recently in Germany on the catalytic action of manganese salts, though calling such substances metallic ferments, shows that Bredig's work has been misunderstood.

W. D. B.

#### Electromotive Forces

On the difference of potential arising at the surface separating two non-miscible liquids each containing the same dissolved electrolyte. *J. J. van Laar. Arch. néerl.* (2) 8, 226 (1903). — When potassium chloride is dissolved in two non-miscible liquids, it is essential that the sum of the potentials for potassium and chlorine as ions shall be the same in the two solutions, but it is not necessary, according to the author, that the potential of potassium as ion or of chlorine as ion must be the same in the two phases. When this is not the case there will obviously be a potential difference between the two phases.

W. D. B.

On the asymmetry of the electrocapillary curve. *J. J. van Laar. Arch. néerl.* (2) 7, 443 (1902). — Reviewed (7, 234) from *Zeit. phys. Chem.* 41, 385 (1902).

#### Electrolysis and Electrolytic Dissociation.

Electrolysis of chloric acid and the chlorates. *A. Brochet. Comptes ren-*

*du*, 138, 200 (1903). — The author gives up the point that the reduction of potassium chlorate, when electrolyzed with a copper anode, is due to the action of copper chlorate on metallic copper. He now recognizes that this was untenable from a quantitative point of view. Brochet now admits the possibility, first suggested by Burrows and made more probable by the corrected analysis, that cuprous chlorate is first formed, which then decomposes into cupric chlorate and cupric oxide. This accounts only for one hundred percent reduction. To get a value of 160 percent, one must also have reduction of chlorate to chloride at the cathode, a point which Brochet has hitherto denied in spite of evidence to the contrary. *W. D. B.*

**Influence of gases on the separation of metals by electrolysis.** *A. Hollard and Bertiaux. Comptes rendus*, 137, 853 (1903). — The authors add sulphur dioxide to a solution of nickel and zinc sulphates plus magnesium sulphate and ammonia. Depolarization by the sulphur dioxide permits a larger current for the same potential difference. Nickel is precipitated quantitatively in an hour at 90° with a current of 0.1 ampere. No test was applied to find out whether the nickel contained magnesium. *W. D. B.*

**Effect of physical nature of anode on the constitution of electrolytic lead peroxide.** *A. Hollard. Comptes rendus*, 138, 142 (1904). — The theoretical percentage of lead in lead peroxide is 86.6. The author has shown (8, 309) that with a platinized anode the percentage of lead in the deposit varies from 74.0 to 86.1, depending on the concentration of the solution. With a platinum anode roughened by the sand blast, the composition of the deposit was independent of the concentration of the solution, but contained only 85.4 percent lead. No details are given so that it is impossible to tell whether this is really due to the formation of a higher oxide or to occlusion. The actual values vary from 85.8 to 84.8, so that it is by no means certain that the composition of the precipitate is independent of the concentration of the solution. *W. D. B.*

**Does the solvent move with the ions during electrolysis?** *C. A. Lobry de Bruyn. Recueil Trav. Pays-Bas*, 22, 430 (1903). — The author has electrolyzed silver nitrate in an aqueous methyl alcohol solution and finds that the ratio of methyl alcohol to water is unchanged both in the cathode chamber and the anode chamber. This would not be the case were one of the ions hydrated. *W. D. B.*

**An experimental law on the electrical transference of dissolved salts.** *A. Ponsol. Comptes rendus*, 138, 192 (1904). — From some experiments by Chassy, made in 1890, the author deduces the law : —

“In the electrolysis of a mixture of salts of the same acid, only one of which is decomposed, the total number of molecules transferred depends only on the nature and concentration of the salt decomposed and is independent of the nature and concentration of the salts which are not decomposed.” The accuracy of Chassy's experiments is not sufficient to justify any such law, especially in view of the fact that there are accurate experiments which disprove this alleged law. *W. D. B.*

**Electrical endosmose in liquid ammonia.** *M. Ascoli. Comptes rendus, 137, 1253 (1903).* — With an alumina diaphragm in liquid ammonia, there is a slight negative endosmose. When sodium is dissolved in the liquid, there is a strong positive endosmose. *W. D. B.*

**The use of alternating currents in electrolysis.** *A. Brochet and J. Petit. Comptes rendus, 138, 359 (1904).* — With an alternating current of 42 alternations, copper dissolves readily in potassium cyanide solution, the yield being high (not given) until the solution is nearly saturated. The authors do not accept the explanation of Le Blanc and Schick that the copper dissolves because it forms a complex ion. Zinc and nickel behave like copper, while lead, silver, mercury and cadmium do not dissolve to any extent. *W. D. B.*

**Reduction with alternating currents.** *F. Pearce and C. Couchet. Comptes rendus, 138, 361 (1904).* — With an alternating current and a high current density there is a very effective reduction of nitrates to nitrites when the electrodes are cadmium or zinc, while there is practically no reduction with electrodes of copper, iron or carbon. *W. D. B.*

**The electrical conductivity of solutions at the freezing-point of water.** *W. C. D. Whelham. Proc. Roy. Soc. 71, 332 (1903).* — Data are given for the conductivity at 0° for solutions of potassium chloride, barium chloride, potassium bichromate, copper sulphate and magnesium sulphate from extreme dilutions up nearly to saturation. *W. D. B.*

**On the electrical conductivity of hydrated nickel sulphate in methyl alcohol solution.** *C. A. Lobry de Bruyn and C. L. Jungius. Recueil Trav. Pays-Bas, 22, 426 (1903).* — There is no measurable time effect in the conductivity of solutions of different hydrated sulphates when dissolved in methyl alcohol. Solutions of hydrated nickel sulphate in methyl alcohol show decreasing molecular conductivity with increasing dilution up to  $M/128$ ; from this point onward the molecular conductivity increases with dilution without showing any signs of approaching a maximum at  $M/4096$ . *W. D. B.*

**The resistance of the ions and the mechanical friction of the solvents.** *F. Kohlrausch. Proc. Roy. Soc. 71, 338 (1903).* — The author makes the following hypotheses: —

"About every ion moves an atmosphere of the solvent, whose dimensions are determined by the individual characteristics of the ion. The atmospheres of multivalent or compound ions differ from those of monatomic ions. Data are at present lacking for a more complete representation.

"The electrolytic resistance of an ion is a fractional resistance that increases with the dimensions of the atmosphere. The direct action between the ion and the outer portion of the solvent diminishes as the atmosphere becomes of greater thickness."

From these premises and from the experimental data the author draws the following conclusions: —

"(a) The electrical resistance of an ion, expressed in mechanical units, must be of the same order of magnitude as the mechanical frictional resistance of a molecule of the solvent; a law whose assumption, as I some time ago

showed, " leads to an expression for the distance between the molecules which is comparable with the usually accepted views in regard to this quantity.

"(b) The empirically discovered law that the temperature change of the resistance of the most sluggish ions is very like the temperature change of the viscosity of water, becomes now understandable. For ions of large resistance we must assume that the atmosphere is of considerable thickness, and hence the action of the ion itself on the outer portion of the solvent will be small. As a limiting case, for a very sluggish ion there will be only the friction of water against water, and the electrolytic resistance will have the same temperature coefficient as the viscosity of water, provided that the atmosphere itself does not change its dimensions with the temperature. If, however, the atmosphere become, for example, smaller with increasing temperature, the temperature gradient of the conductivity might be greater than that of the fluidity. According to the observations now at hand, this would seem to be the case for the slowest moving univalent ion Li. Even here, however, the differences scarcely exceed the errors of observation.

"(c) I now come to the remarkable relationship between the mobility of the ions and their temperature coefficients, which was mentioned in Section 8. This first led me to seek a general explanation for the electrolytic resistance in the idea of a water atmosphere, in order to escape being compelled to explain this otherwise unreconcilable fundamental characteristic of the ions as a *deus ex machina*.

"Assuming as the single fundamental characteristic of each univalent monatomic ion the formation of a water atmosphere, which varies according to the nature of the ion, the mobility of this complex on the one side, and its temperature coefficient on the other, will be functions of these atmospheric formations, and therefore both quantities must hold functional relations to each other. We know too little of the molecular forces at present to attempt to describe this connection more exactly. But for the case in which the water shell is so thick that the ion exerts no force beyond it, the resistance to motion becomes simply a matter of water friction, which explains the fact that the most sluggish ions have nearly the same temperature coefficients as the viscosity. In the case of smaller aggregations, we must remain content with the fact that we have at least the possibility of a fundamental explanation.

"There are two experimental questions which are of importance, although difficult to answer: first, whether the functional relationship is exact or only approximate, and second, whether the positive and negative ions are fully identical in regard to this relationship.

"That the non-elementary ions also show as their greatest temperature coefficients that of water friction, but that they as groups differ from the elementary ions, is to be expected. The latter fact cannot be quantitatively explained. Here also it will be necessary to wait for more exact experimental data to settle the question.

"(d) Finally, the indication of the temperature formula that the mobility of all the ions converges toward zero at about the same temperature, is a logical result, if the electrolytic resistance is in reality a mechanical friction. The fact that the formula for the fluidity of water takes part in this convergence, gives the hypothesis further support.



"It does not seem at all impossible that the deviations from a strictly common zero point, found in extrapolating the different formulæ, have a systematic cause. These divergences seem to indicate that the more mobility an ion shows at ordinary temperatures, the more slowly relatively it loses the residue of its mobility as the solvent becomes more viscous. The mobility of the water molecules themselves becomes small at a comparatively high temperature, where such ions as K, Cl, NO<sub>3</sub>, SO<sub>4</sub>, and even more, OH and H still possess a considerable residue of electrolytic mobility. Such a relationship does not seem at all improbable.

"In the foregoing pages I have sought to find a cause for the electrolytic resistance in the single fundamental characteristic of the ions, their hydration, that is, their ability to form atmospheres from the solvent. These views form a hypothetical sketch for the completion of which much is still wanting. It appears to me, however, complete enough to invite one to its experimental or theoretical continuation."

W. D. B.

The theory of electrolytic dissociation. *W. C. D. Whetham. Phil. Mag.* [6] 5, 279 (1903). — A discussion of the present status of the electrolytic dissociation theory. The conclusion is reached, though not formulated, that the possible mutual effects of electrically charged ions are sufficiently important to make it impossible for us to predict anything quantitative in regard to any except completely dissociated solutions.

W. D. B.

Theory of amphoteric electrolytes. *J. Walker. Proc. Roy. Soc.* 73, 155 (1904). — The author discusses the equilibrium relations for amphoteric electrolytes and shows "that the electrical conductivity when treated in the ordinary way forms no measure of the acidity or even of the ionization of the dissolved electrolyte." It is further shown that an amphoteric electrolyte cannot follow Ostwald's dilution law, unless either the basic or acid dissociation constant is negligible with reference to the dissociation constant of water. As a matter of fact Winkelblech found that the electrolytes studied by him did not follow the dilution law. It is further believed that conclusions based on catalytic experiments with the hydrochloride of an amphoteric electrolyte are more trustworthy than those based on conductivity measurements with the same substance.

W. D. B.

The color of aqueous solutions of methyl orange and the change produced by acids. *P. Vaillant. Comptes rendus*, 137, 849 (1903). — The molecular absorption of methyl orange is independent of the concentration. The molecular conductivity of methyl orange is more than half that of hydrochloric acid. Attention is also called to the fact that weak acids in concentrated solutions affect methyl orange. From these facts the author concludes that both dissociated and undissociated salt are yellow and that the color change is due to a chemical reaction.

There is nothing to show whether the author studied the sodium salt of methyl orange or not. There is no reference to the fact that the sulphonic acid group is not essential to the color, and the author is not familiar with Waddell's work.

W. D. B.

*Dielectricity and Optics*

On the oxidizing action of the rays from radium bromide as shown by the decomposition of iodoform. *W. B. Hardy and E. G. Willcock. Proc. Roy. Soc. 72, 200 (1903); Zeit. phys. Chem. 47, 347 (1904).* — When iodoform is dissolved in chloroform, traces of oxygen plus some form of radiant energy will set free iodine. This decomposition takes place under the influence of sunlight or even of a yellow gas flame. It is found that the  $\alpha$ -radium rays have no effect, while the  $\beta$ - and  $\gamma$ -rays produce decomposition, the  $\beta$ -rays being the more effective of the two. Röntgen rays also cause decomposition. *W. D. B.*

Experiments in radioactivity and the production of helium from radium. *W. Ramsay and F. Soddy. Proc. Roy. Soc. 72, 204 (1903); Zeit. phys. Chem. 47, 490 (1904).* — The discharging power of the radium emanation is entirely unaffected by sparking with oxygen over alkali, or by exposure to heated magnesium powder and lime. The authors confirm the experiments of Rutherford and Soddy that the emanation can be dealt with as a gas. The maximum amount of the emanation obtained from 50 milligrams of radium bromide was condensed by liquid air and sealed in a vacuum tube. The tube then showed no signs of the helium spectrum. After standing for four or five days the helium spectrum appeared. Helium was also shown to be present in the gases produced by the direct action of radium bromide on water. *W. D. B.*

Change of the electrical resistance of selenium under the influence of certain substances. *A. B. Griffiths. Comptes rendus, 137, 647 (1903).* — The electrical resistance of selenium diminishes markedly when exposed, at a distance of 5 cm, to the alcoholic solutions of a number of plant and animal pigments. The conclusion to be drawn is that these solutions emit rays. *W. D. B.*

Action of radium bromide on the electrical resistance of bismuth. *R. Faillot. Comptes rendus, 138, 139 (1904).* — A spiral of bismuth between two mica plates was exposed to the radiation from 0.03 g radium bromide (activity 500,000) enclosed in a glass tube. The resistance of the spiral is decreased when the radium bromide is close to it, but the effect becomes practically zero at a distance of 1 cm. There seems to be no time factor. *W. D. B.*

Contact electrification and theory of colloidal solutions. *J. Perrin. Comptes rendus, 137, 564 (1903).* — It is believed that colloidal solutions are formed of electrically charged granules, invisible in the microscope, but much larger than the molecules. To account for a stable equilibrium with particles of a definite diameter, the following hypothesis is put forward. "The surface tension and cohesion favor the growth of a granule; but the electrification of this granule tends to disrupt it. The balance of these two tendencies determines the diameter of the granule." *W. D. B.*

Abnormal changes in some lines in the spectrum of lithium. *H. Ramage. Proc. Roy. Soc. 71, 164 (1903).* — "The lines in the principal series of lithium appear to broaden and reverse normally. The lines in the second subordinate series do not reverse even in the arc, but in strong arcs they broaden towards the less refrangible end of the spectrum and become diffuse on that side."

"The first line in the first subordinate series, wave-length 6103.84, is almost normal; it broadens slightly more on the more refrangible side than on the other. The other lines in this series also broaden on both sides and become diffuse, but they broaden more rapidly on the more refrangible side than on the other. The centers of the broadened lines are more refrangible than the corresponding lines in the narrow state. The inner core of intense arcs, and the parts near the negative poles of weak arcs and sparks, give a broad reversed line with its center about wave-length 4602.4; while the part near the positive pole in weak arcs, and the flame of the arc, give a sharp bright line, wave-length 4603.07, coincident with the lines in the spectra of the oxyhydrogen flame and uncondensed spark. The similar changes in the other lines diminish with their refrangibility. The wave-lengths hitherto recorded for these diffuse lithium lines would appear to be those of abnormal lines. The true lines are the sharp bright ones which occur, without complication, in the spectrum of lithium in the oxyhydrogen flame.

W. D. B.

The spectra of metallic arcs in an exhausted globe. A. Fowler and H. Payn. *Proc. Roy. Soc.* 72, 253 (1903). — "So far as they go, the experiments seem to suggest that the modification of the arc spectra in an exhausted globe may be due to the presence of hydrogen liberated from the heated poles. It has already been pointed out that one of the effects of a hydrogen atmosphere on a metallic arc is to introduce enhanced lines into the spectrum, and the presence of hydrogen under the new conditions of experiment is indicated in the case of magnesium and zinc by the appearance of the  $H\beta$  line, and in magnesium, zinc, and cadmium by flutings which are known to appear in the presence of hydrogen.

"It is well known that hydrogen is occluded by many metals, and experiments made to determine the relative amounts of the gas given off on heating *in vacuo* show that the amounts are roughly proportional to the relative strengths of the enhanced lines appearing when the arc passes in the exhausted globe; that is, magnesium and zinc gave off the greatest quantities of the gas, cadmium the least, and iron an intermediate amount. The apparent absence of the F line in the spectra of cadmium and iron in the exhausted globe may, therefore, be due to its feeble intensity on account of the smaller quantity of gas driven out, while the absence of "hydride" bands in the case of iron may perhaps be explained by supposing that combination of hydrogen with iron does not readily take place.

"The exact nature of the action of hydrogen on the arc requires further investigation."

W. D. B.

The ultra-violet spectrum of radium. W. Crookes. *Proc. Roy. Soc.* 72, 295, 413 (1903). — The author gives tables of the lines in the ultra-violet spectrum of radium as found by him and by others. He also gives collotype reproductions from his negatives.

W. D. B.

On the spectrum of the spontaneous luminous radiation of radium at ordinary temperatures. W. Huggins and Lady Huggins. *Proc. Roy. Soc.* 72, 196, 409 (1903). — The spectrum of the light emitted by radium was too faint to be studied by a direct vision method. With a quartz prism and an exposure of

seventy-two hours, a photograph was obtained. It was found that the strongest seven lines agree in position, relative intensity and character with bands of the spectrum of nitrogen. The spectrum differs radically from the spark spectrum of radium. In the second paper the coincidence of the radium bromide glow spectrum with the band spectrum of nitrogen is shown to be even more complete.

W. D. B.

On the light emitted spontaneously by certain uranium salts. *H. Becquerel. Comptes rendus*, 138, 184 (1904). — Samples of the double uranyl and potassium sulphate were found to emit light spontaneously and apparently indefinitely. The most light was emitted by the most phosphorescent preparations. A radium preparation with a radio-activity one million times that of the uranium salt, emitted only twenty thousand times as much light. The light from the double sulphate is apparently the same spectrally as the phosphorescent light from the same substance.

W. D. B.

The phosphorescence of calcium sulphide containing bismuth and prepared in presence of traces of sodium. *L. E. O. de Visser. Recueil Trav. Pays-Bas*, 22, 133 (1903). — Calcium sulphide made from pure marble would not give, on addition of bismuth, the phosphorescence that was obtained by starting with commercial calcium carbonate. It was found that the difference was due to the presence of sodium carbonate in the commercial calcium carbonate. A special series of experiments showed that the maximum phosphorescence was obtained when there were about sixty combining weights of sodium and one of bismuth to fifty thousand of calcium.

W. D. B.

The emanations of radium. *W. Crookes. Proc. Roy. Soc.* 71, 405 (1903). — When radium is brought near a zinc sulphide screen, the latter begins to scintillate, the "flashes following each other so quickly that the surface looks like a turbulent sea". "It seems probable that in these phenomena we are actually witnessing the bombardment of the screen by the electrons hurled off by radium with a velocity of the order of that of light, each scintillation rendering visible the impact of an electron on the screen." [The apparatus for showing this phenomenon is now known as the spinthariscopes.]

W. D. B.

On the scintillating phosphorescence produced in some substances by the rays of radium. *H. Becquerel. Comptes rendus*, 137, 629 (1903). — This is a study of the spinthariscopes. By using different screens and by interposing different substances between the screens and the radium salts, the author succeeds in showing that the spinthariscopes effect is due to the  $\alpha$ -rays and that the  $\beta$ -rays have little or no effect in producing it. It was noticed that the scintillations were more intense, the smaller the crystals of the zinc blende used as a screen and it was shown that similar scintillations are seen when zinc blende is crushed mechanically in the dark.

W. D. B.

Note on the effect of extreme cold on the emanations of radium. *W. Crookes and J. Dewar. Proc. Roy. Soc.* 72, 69 (1903). — When a radium salt at the temperature of liquid air is brought close to a zinc sulphide screen at ordinary temperatures, a vigorous scintillation is observed. When the screen is at the temperature of liquid air and the radium at the ordinary temperature,

the scintillations cease entirely if there is no water present. With water present, the temperature effect disappears. *W. D. B.*

The effects of heat and of solvents on thin films of metal. *G. T. Beilby. Proc. Roy. Soc. 72, 226 (1903).* — Faraday showed in 1857 that thin films of metal on glass become more transparent and poorer conductors of electricity when annealed. The author has confirmed this and has also found that all mechanical disturbance of the surface by polishing or burnishing tends to diminish transparency and to increase the reflecting power.

On annealing films there is a tendency to aggregate into granules, leaving the intervening portions thinner, but this is not the sole cause of the increased transparency. The electrical resistance of these films changes from a few ohms before heating to thousands of megohms after annealing.

"When a gold leaf laid on glass by Faraday's method is exposed for a very short time to mercury vapor, minute globules of mercury condense on the surface and, amalgamating with the gold, form transparent spots. The transparency quickly spreads and the whole leaf becomes almost as transparent and free from metallic reflection as if it had been annealed by heat." *W. D. B.*

#### *Crystallography, Capillarity and Viscosity*

The polymorphism of the nitrates. *F. Wallerant. Comptes rendus, 137, 805 (1903).* — Ammonium nitrate can be made to crystallize in five of the six systems. Caesium nitrate is cubic at its melting-point. At a lower temperature there is a triple point below which are rhombohedral crystals. On cooling these rhombohedral crystals to  $-180^{\circ}$  they pass continuously without the intervention of a triple point into cubic crystals. *W. D. B.*

Spontaneous crystallization of gypsum. *S. Meunier. Comptes rendus, 137, 942 (1903).* — After being soaked in salt water and then allowed to dry, some masses of plaster were observed to crystallize in fairly large crystals. It is suggested that the cause of the crystallization is the salt. *W. D. B.*

Surface flow in crystalline solids under mechanical disturbances. *G. T. Beilby. Proc. Roy. Soc. 72, 218 (1903).* — When a crystalline metal like antimony is polished, the surface becomes apparently amorphous and has all the appearance of a viscous liquid. Iceland spar shows the effect of direct pressure in an unmistakable change of surface, while the effect of a single polishing stroke can be detected by a subsequent etching of the surface.

In burnishing or planishing metal on a smooth surface, the flow is not so strictly confined to the surface nor to the exact spot at which the pressure is applied, as it is in the case of hard, brittle substances. In the softer metals the flow proceeds much further from the center of pressure than it does in the harder. Very minute crystalline fragments of antimony or bismuth can be beaten into scales, and their flow appears to be as perfect as that of gold or silver. As the size of the particles is increased, the outer edge of the minute plates develops notches and radial cracks showing that the limit of flow has been exceeded. *W. D. B.*

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==THE==  
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[ Continued on closing pages. ]

# MOLECULAR ATTRACTION

(SECOND PAPER)

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BY J. E. MILLS

## Review of the Theory

This paper presents additional evidence tending to show that the attraction between molecules varies inversely as the square of their distance apart and does not vary with the temperature. Considering the attraction as a property belonging to each molecule, or to be more exact, a mutual property of each pair of molecules, it must vary as the mass, large numbers of similar molecules being here considered. Briefly therefore this paper is an attempt to show that the *law of gravitation* holds, not only between masses, but between the molecules of a substance, and that this law is alone sufficient to account for the phenomena of the internal latent heat of vaporization.

The assumptions upon which the present work is based are stated in the original paper,<sup>1</sup> and it would not be necessary here specifically to call attention to them were it not for the fact that certain reviews have overlooked the significance of the preliminary statements to that paper. We may say that the steps leading up to the present work are briefly:—

1. The kinetic theory of gases and van't Hoff's application of the gas law  $PV = RT$  to solutions.
2. The conclusion from the above theories and related work that the average translational energy of gaseous and liquid molecules must at the same temperature be equal.
3. The belief based on the study of the specific heat of gases, that the *total* energy of a gaseous molecule, exclusive of the energy which holds the molecule together and of extraneous forces, is proportional to the translational energy.
4. The inference, for it is somewhat more than a mere assumption, the causes for 3 being considered, that the *total* energy

---

<sup>1</sup> Jour. Phys. Chem. 6, 209 (1902).

of a molecule of a liquid would similarly be found to be proportional to its translational energy.

These four preliminary steps may be summed up by the statement that the total energy *per se* of a molecule must be the same in the liquid as in the gaseous state, the temperature being the same. If at a given temperature a given weight of gas represents more energy than the same weight of the substance as a liquid, the extra energy of the gas must be energy of position only (assuming no intramolecular change).

We made no attempt in the former paper, and we make none in this, to prove the last statement above, or to give the evidence for it. To do so even cursorily would require a discussion of the kinetic theory of gases, their specific heats more particularly, and the modern theories of solution. The statement is here made only as the belief of the author upon which the present work is based. Many citations of closely related belief might be given. Ostwald<sup>1</sup> gives a clear and succinct statement of 1 and 2. O. E. Meyer<sup>2</sup> shows the grounds for 3. The author has published<sup>3</sup> the study which led him to conclude that 4 was a reasonable supposition. So long ago as 1885, Ramsay and Young made practically the same statement.<sup>4</sup>

Expressing the above belief in a different form, we may say that the energy necessary to change a liquid into a gas must then be spent solely in overcoming the external pressure and in altering the distance apart of the molecules. (Unless the molecule breaks apart also or nears the point of disruption.)

Denoting the energy spent in overcoming the external pressure by  $E_1$ , this energy can be calculated from the equation,

$$(1) \quad E_1 = 0.031833 P(V - v) \text{ cal},$$

where the unit calorie is from 15° to 16° C, P is the pressure

<sup>1</sup> Solutions, pp. 147, 148.

<sup>2</sup> Kinetic Theory of Gases, p. 117.

<sup>3</sup> Journal of the Elisha Mitchell Scientific Society, Vol. 13 (1902).

<sup>4</sup> Phil. Trans. 1886A, Evaporation and Dissociation, p. 72, Section 4;  $c$  and  $d$  of that section not being necessary under the limitation imposed above that there should be no intramolecular change, and  $e$  and the footnote being unnecessary in the light of the later work of van 't Hoff.

in millimeters of mercury,  $V$  and  $v$  are the volumes before and after expansion. To obtain the constant, 0.031833, we used the values: density of mercury, 13.5956; Rowland's value of the therm, corrected by Day, at 15° to 16° C, 41880000 ergs, as unit; and gravity taken as 980.5966.

Denoting the total latent heat by  $L$ , we have  $L - E_i$  as the energy spent in overcoming the molecular attraction at any particular temperature.

On the further assumption:—

5. That the molecular attraction varies inversely as the square of the distance apart of the molecules, the equation 7 (p. 212) of the original paper was derived, which equation readily takes the more convenient form,

$$(2) \quad \frac{L - E_i}{\rho/d - \rho/D} = \text{constant},$$

for any particular substance, where  $L - E_i$  is the internal latent heat of vaporization, and  $d$  and  $D$  are the densities of liquid and vapor at any particular temperature.

With regard to this equation, we will here say that it was designed to test the assumption advanced in 5. Had it failed to produce a constant or some function of the temperature, the author hoped to substitute 5 by some other distance function of the attraction, obtain the formula similarly, and thus repeat until the correct assumption was made.

As to the mathematics by which it was derived, the vagaries of a particular molecule cannot of course be followed. But in considering energy relations we commit no error by considering the average molecule as was done. The formula should therefore hold strictly true provided:—

- (a) The molecules are evenly distributed.
- (b) The number of molecules does not change.
- (c) No energy is spent in intramolecular work.
- (d) The attraction does not vary with the temperature.

Or, we might sum up  $a$ ,  $b$ ,  $c$ , and  $d$ , by saying that formula 2 should hold, provided we are dealing with a stable chemical compound whose molecules are not associated.



The first paper tested the formula so far as the direct measurements of latent heat and the related data permitted. The agreement appeared to be much too close to be the result of accident, but where variations in the data as given by different observers amounted often to five and ten percent, any close agreement was impossible. It being impracticable to make direct measurements of the latent heat at widely different temperatures, attention was called to the measurements of Ramsay and Young and of Dr. Young. These measurements give the vapor pressure and density of liquid and vapor, at corresponding temperatures over a wide range of temperature for thirty-one substances. The present paper deals with twenty-one of these substances, the calculations for the ten esters being not yet completed.

#### **The Measurements.**

The complete measurements used are given in the appended tables.

The few exceptions to the following general statements are noted below.

(a) The vapor pressure, density of the liquid, and density of the vapor, are from the measurements, references given below, by Professors Ramsay and Young, or Young.

(b) The vapor pressures from Biot's formula were used in preference to the observed values.

(c) Where calculated the density of the vapor was obtained from the formula.

$$(3) \quad D = 0.0416016 \frac{Pm}{T},$$

where  $P$  is the pressure in millimeters of mercury,  $m$  is the molecular weight, oxygen equal to 16 as standard, and  $T$  is the absolute temperature. The constant 0.0416016 was obtained by the use of the values 0.0489873 for the density of hydrogen at  $0^{\circ} \text{C}$ , 760 mm pressure, latitude  $45^{\circ}$  and sea level, and  $0^{\circ} \text{C} = 273^{\circ}$  absolute.

(d) The densities of the vapor given are often carried one place further than the accuracy of the measurements would war-

rant. This was because the density of the vapor was not always given directly in the original paper, and in the necessary transposition the additional figure of the calculation was retained.

(e) Making use of the well-known thermodynamic equation,

$$(4) \quad L = \frac{\partial P}{\partial T} \frac{T}{J} (V - v),$$

the latent heat of vaporization for methyl, ethyl and propyl alcohols, acetic acid, and ether, were calculated and given in the original papers, where the method in detail may be obtained. The latent heat for water,  $0^{\circ}$  to  $230^{\circ}$  C, is from Regnault. The latent heat for benzene,  $0^{\circ}$  to  $270^{\circ}$  C, is from Tsuruta,<sup>1</sup> using measurements of Young.

(f) In all other cases the latent heats were calculated by the author, the following method being used. Biot's general formula for the vapor pressure,

$$(5) \quad \log P = a + ba' + c\beta',$$

has been found with properly chosen constants accurately to represent the vapor pressure. Differentiating and changing base of the logarithms from natural to Naperian we get :

$$(6) \quad \frac{\partial P}{\partial T} = \frac{P}{m} (b \log aa' + c \log \beta\beta'),$$

where  $m = 0.434294$ . Substituting this value of  $\frac{\partial P}{\partial T}$  in equation 4, we get :

$$(7) \quad L = 5.3019 \frac{P(V-v)T}{J} (b \log aa' + c \log \beta\beta');$$

and using values for  $P$  and  $J$  already adopted (p. 385), we have finally :

$$(8) \quad L = 0.0168775 P \Delta v T (b \log aa' + c \log \beta\beta') \text{ cal; or}$$

$$(9) \quad L = \frac{P \Delta v T}{10^6} A \text{ cal, if,}$$

$$(10) \quad A = 168775 (b \log aa' + c \log \beta\beta').$$

<sup>1</sup> Phys. Rev. 10, 2 (1900).

In this form the calculation of the latent heat is not only theoretically correct, but is much shortened in comparison with the usually adopted methods. The values for A were obtained from the constants for Biot's formula given in the original papers, and the equations thus derived for each substance are given below under that substance.

(g) All calculations in this paper were checked and every effort was made to make the calculations as accurate as the data from which they were derived.

*Ether.* See Table 2. Data from Phil. Trans. 1887A, p. 57; except density of liquid at 10°, 20° and 30° C, where the values are from Oudemans. Molecular weight used 74.08.

*Di-isopropyl.* See Table 3. Data from Jour. Chem. Soc. 1900, p. 1126, except vapor pressure at 216° and 225° C (calculated from Biot's formula); and vapor density at 0° C which is theoretical. Molecular weight used, 86.112. For calculation of the latent heat,

$$A = \text{antilog} (\overline{1.572552} - 0.00020800t) \\ + \text{antilog} (0.1268648 - 0.00466932t),$$

where  $t = t^\circ \text{C} + 10$ .

*Di-isobutyl.* See Table 4. Data from Jour. Chem. Soc. 1900, p. 1136, except vapor pressure at 274° C (calculated from Biot's formula); and vapor density at 0° C which is theoretical. Molecular weight used, 114.144. For calculation of the latent heat,

$$A = \text{antilog} (\overline{1.1739925} + 0.00104426t) \\ + \text{antilog} (0.2271234 - 0.00380225t),$$

where  $t = t^\circ \text{C} - 10$ .

*Isopentane.* See Table 5. Data from Proc. Phys. Soc. 1895, p. 602; except vapor density at 0° C which is theoretical. Molecular weight used, 72.10. For calculation of the latent heat we have,

$$A = \text{antilog} (\overline{1.6310169} - 0.00031549t) \\ + \text{antilog} (0.1373762 - 0.00515903t),$$

where  $t = t^\circ \text{C} + 30$ .

*Normal Pentane.* See Table 6. Data from Jour. Chem. Soc. 21, 1897, p. 446; except vapor density at 0° C which is theoretical. Molecular weight used is 72.10. For calculation of the latent heat, we have,

$$A = \text{antilog} (\bar{1.7496468} - 0.00073363t) \\ + \text{antilog} (0.0668185 - 0.00551392t),$$

where  $t = t^\circ \text{C} + 20$ .

*Normal Hexane.* See Table 7. Data from Jour. Chem. Soc. 1895, p. 1071; except vapor density at 0° C which is theoretical. Molecular weight used is 86.11. For calculating the latent heat, we have,

$$A = \text{antilog} (\bar{1.3604438} + 0.00042355t) \\ + \text{antilog} (0.2029359 - 0.00411255t),$$

where  $t = t^\circ \text{C} + 10$ .

*Normal Heptane.* See Table 8. Data from Jour. Chem. Soc. 74, 1898; except vapor density at 0° C which is theoretical, and vapor pressure at 266° and 266.5° C which is calculated from Biot's formula. The molecular weight used is 100.13. For calculation of the latent heat, we have,

$$A = \text{antilog} (\bar{1.3407071} + 0.00053408t) \\ + \text{antilog} (0.2342860 - 0.00403623t),$$

where  $t = t^\circ \text{C}$ .

*Normal Octane.* See Table 9. Data from Jour. Chem. Soc. 1900, p. 1145; except vapor density at 0° C which is theoretical. The molecular weight used is 114.144. For calculation of the latent heat, we have,

$$A = \text{antilog} (\bar{1.3927781} + 0.000342913t) \\ + \text{antilog} (0.2497609 - 0.004006534t),$$

where  $t = t^\circ \text{C} - 10$ .

*Benzene.* See Table 10. Data from Jour. Chem. Soc. 1889, p. 501; except density of vapor at 0° C which is theoretical. Molecular weight used is 78.05. Latent heats were calculated by Tsuruta (Phys. Rev., 1900, p. 116), except at 0° C, where the value found by Griffiths and Marshall is used, and at 280° C where the calculation was made by the author.

*Hexamethylene.* See Table 11. Data from Jour. Chem. Soc. 1899, p. 873; except vapor density at 0° C which is theoretical. Molecular weight used is 84.096. For calculation of the latent heat, we have,

$$A = \text{antilog} (\bar{1}.2956115 + 0.00049715t) \\ + \text{antilog} (0.1878242 - 0.00391252t),$$

where  $t = t^\circ \text{ C}$ .

*Fluo-benzene.* See Table 12. Data from Jour. Chem. Soc. 21, 1889, p. 505; except the vapor density at 0° C which was calculated. Molecular weight used is 96.09. For calculation of the latent heat, we have,

$$A = \text{antilog} (\bar{1}.13157974 + 0.000942654t) \\ + \text{antilog} (0.2224140 - 0.00363024t),$$

where  $t = t^\circ \text{ C}$ .

*Chlor-benzene.* See Table 13. Data from Jour. Chem. Soc. 1889, p. 502; except vapor density at 0° C which is theoretical. The molecular weight used is 112.5. For calculating the latent heat, we have,

$$A = \text{antilog} (\bar{1}.2268791 + 0.00075845t) \\ + \text{antilog} (0.1846519 - 0.00359227t),$$

where  $t = t^\circ \text{ C} - 30$ .

*Iodo-benzene.* See Table 14. Data from Jour. Chem. Soc. 1889, p. 506; except vapor density at 30° and 100° C which is theoretical. Molecular weight used was 203.9. For calculating the latent heat, we have,

$$A = 0.09891873 \{ \text{antilog } 0.001421982t \\ + \text{antilog } 1.28759778 - 0.00324574t \} ,$$

where  $t = t^\circ \text{ C} - 30$ , a form of the equation less convenient for calculation than the one usually adopted.

*Brom-benzene.* See Table 15. Data from Jour. Chem. Soc. 1891, p. 134; except vapor density at 30° and 100° C which is theoretical. Molecular weight used was 157.0. For calculation of the latent heat, we have,

$$A = \text{antilog} (\bar{1}.8373717 - 0.00095092t) \\ + \text{antilog } 0.0763464 - 0.00489465t),$$

where  $t = t^\circ \text{ C} - 30$ .

*Carbon Tetrachloride.* See Table 16. Data from Jour. Chem. Soc. 1891, p. 911; except vapor density at 0° C which is theoretical. Molecular weight used was 153.8. For calculation of the latent heat, we have,

$$A = 0.2358 \{ \text{antilog } 0.0002685t \\ + \text{antilog } (0.7970507 - 0.00402434t) \},$$

where  $t = t^\circ \text{ C}$ , a less satisfactory form of the equation than the one usually adopted.

*Stannic Chloride.* See Table 17. Data from Jour. Chem. Soc. 1891, p. 911; except density of the vapor at 0° C which is theoretical, the molecular weight used being 260.8. For calculating the latent heat, we have,

$$A = \text{antilog } (1.3282379 + 0.00026212t) \\ + \text{antilog } (0.2481708 - 0.00368282t),$$

where  $t = t^\circ \text{ C}$ .

*Water.* See Table 18. See Phil. Trans. 1892, p. 107. Vapor pressures, 0° to 100° C, are Broch's calculations from Regnault's measurements, and other values are from Ramsay and Young. Density of the liquid, 0° to 100° C are from values in Landolt and Bornstein's tables, p. 39, and 100° to 270° C are from Ramsay and Young. Density of vapor, 0° to 220° C are as given by Ramsay and Young from Regnault's heats of vaporization, and 230° to 270° "are recalculated" values from their own measurements. Latent heats, 0° to 230° C are from Regnault, and 240° to 270° C were calculated by the author from the formula,

$$A = \text{antilog } (0.1416514 - 0.005950708t) \\ + \text{antilog } (0.13884017 - 0.001656138t),$$

where  $t = t^\circ \text{ C} + 20$ , the constants used for Biot's formula being given by Regnault.

*Methyl Alcohol.* See Table 19. Data from Phil. Trans. 1887A, p. 313; except density of liquid at 0° C from Dittmar and Fawsitt, and at 10° C average value of 0° and 20°. Inadvertently the observed pressures were used for the calculation of  $E_1$ , but the difference thus made is never more than 0.1 to 0.2 calorie, and the error thus introduced into the constant of equation 2 could never exceed one-tenth of one percent.

*Ethyl Alcohol.* See Table 20. Data from Phil. Trans. 1889A, p. 123; except vapor pressure at  $241^{\circ}$ ,  $242^{\circ}$ , and  $242.5^{\circ}$  C (calculated from Biot's formula); density of liquid  $0^{\circ}$  to  $30^{\circ}$  and at  $100^{\circ}$  Mendelejeff,  $40^{\circ}$  to  $80^{\circ}$  from Kopp's formula, and at  $90^{\circ}$  C estimated value.

*Propyl Alcohol.* See Table 21. Data from Phil. Trans. 1889A, p. 137. Observed vapor pressures were used to calculate  $E_v$ . Density at  $0^{\circ}$  C is theoretical, the molecular weight used being 60.06.

*Acetic Acid.* See Table 22. Data from Jour. Chem. Soc. 49, 1886, p. 790, and in 1891, Vol. 59, p. 903, preference being given in all cases to the later measurements. For calculating the latent heat, we have,

$$A = \text{antilog} (\overline{1.9257964} - 0.00149898t) \\ + \text{antilog} (\overline{1.1390566} - 0.0130424t),$$

where  $t = t^{\circ} \text{ C} - 120$ .

#### Application of the Theory

For details of the calculations involved the appended tables, 2 to 22, must be consulted. A summary of the results obtained for the constant by the use of the equation

$\frac{L - E_v}{\frac{1}{\rho_d} - \frac{1}{\rho_D}} = \text{constant}$ , is given below in Table 1. Certain mean values of this constant somewhat arbitrarily chosen are given at the top of each column. All results not in agreement with this mean value of the constant by as much as two percent are in italics.

Since from  $0^{\circ}$  C to within  $10^{\circ}$  of the critical temperature eleven of the substances show altogether, out of two hundred and seventeen observations, only two divergences greater than two percent from the average values, it is clearly evident that the relation given by the equation cannot possibly be accidental. But *is the relation in these and in the other cases as accurate as the excellent experimental data will permit?* Only by such an agreement could the theory be finally established. To answer this question we must examine the manner and ex-

tent to which errors in the observations will affect the constant.

A cursory examination of the equation  $\frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant}$ , would make it appear that as the critical temperature is approached and  $d$  approaches  $D$  in value, the diminishing difference of their respective cube roots would enormously increase the proportional errors of the observations. This is however not the case. Substituting for  $L$ , its value from equation 4 and for  $E_1$ , its value from equation 1, we have,

$$(11) \quad \frac{0.0431833 (V - v) \left( \frac{\partial P}{\partial T} T - P \right)}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant}.$$

Next putting  $d = 1/v$  and  $D = 1/V$ , and simplifying, we get,

$$(12) \quad 0.0431833 (Vv^{2/3} + V^{2/3}v + V^{1/3}v^{2/3}) \left( \frac{\partial P}{\partial T} T - P \right) = \text{constant}.$$

On inspection of the factor,  $Vv^{2/3} + V^{2/3}v + V^{1/3}v^{2/3}$ , we see:

1. That errors of observation occurring in the *density of the liquid* have at low temperatures little effect on the constant, but as the critical temperature is approached and  $v$  approaches  $V$  in value, a percentage error in the density of the liquid will cause about  $\frac{2}{3}$  of the same percentage error in the constant.

2. That errors of observation occurring in the *density of the vapor* cause at low temperatures about the same percentage errors in the constant, but as  $V$  approaches  $v$  the percentage error caused in the constant is decreased to about  $\frac{1}{3}$  of the error of the observation.

To determine the error caused by an error in the vapor pressure, we transform equation 12 into the form

$$(13) \quad \frac{\partial P}{\partial T} T - P = \frac{\text{Constant}}{0.0431833 (Vv^{2/3} + V^{2/3}v + V^{1/3}v^{2/3})}.$$

The right-hand side of the equation is very small at low temperatures, but increases with rise of temperature until as the critical temperature is approached the function of the volumes approaches  $3V^{1/3}$ .

The relative magnitude of the terms on the left-hand side of



the equation must be considered. Taking water at  $0^{\circ}$  C as typical of a low vapor pressure (that it is typical will be seen if other substances are examined), we have  $\frac{\partial P}{\partial T} = 0.329$ ,  $T = 273$ ,  $P = 4.600$ ,  $V = 211131$ ,  $v = 1$ , and the equation takes the form  $0.329 \times 273 - 4.600 = \frac{\text{Constant}}{0.031833 \times 214737}$ . Since  $0.329 \times 273 = 89.80$ , the influence upon the constant of an error in the vapor pressure is relatively very small.  $T$  may be assumed correct, and the determining error therefore rests with the  $\frac{\partial P}{\partial T}$ . It is exceedingly important to note that while an error of 0.01 millimeter in the vapor pressure is an error of only *two-tenths of one percent* in that observation, yet if the same error exists in the  $\frac{\partial P}{\partial T}$  the error so caused in the constant is *three percent*.

For high vapor pressure considering water at  $270^{\circ}$  C (also a typical case) we have  $\frac{\partial P}{\partial T} = 614$ ,  $T = 543$ ,  $P = 40570$  (from Biot's formula as given by Regnault), and the equation takes the form  $614 \times 543 - 40570 = \text{etc.}$  And since  $614 \times 573 = 351800$ , it again appears that an error in the pressure produces only a very greatly diminished proportional error in the constant. It is again important to note that while an error of 20 millimeters in the pressure means an error of only *0.05 of one percent* in that measurement, yet this error occurring in the  $\frac{\partial P}{\partial T}$  would produce an error of *more than three percent* in that constant.

The function  $\frac{\partial P}{\partial T}$  was obtained from Biot's formula (see equation 5). Biot's formula has stood the most severe tests, and I do not believe the accuracy of that formula *per se* can now be questioned.<sup>1</sup> But it is a purely empirical formula *fitted* to the observations. It represents a curve and primarily is but a more refined method of drawing a curve through the observations.

<sup>1</sup> See Ramsay and Young. Phil. Trans. 1887A, p. 82.

For all points along the line of this curve one is guided by the observations on *either* side until the ends of the curve are approached. But as the ends of the curve are approached one has to be guided more and more by the trend of the curve already established. That is, *along interior portions of the curve individual errors in the measurement of the pressure are smoothed out and Biot's formula is far more accurate than the individual measurements, but at the ends of the curve this smoothing is necessarily far more imperfect and Biot's formula cannot give greatly more accurate results than the individual observations.* (The fact that the constants for the formula are mathematically calculated makes this observation of course none the less true.)

Individual observations of vapor pressure could not be used to obtain a correct idea of the  $\frac{\partial P}{\partial T}$  *because an error in these observations is multiplied proportionately anywhere from ten to seventy times in the  $\frac{\partial P}{\partial T}$ .* The method adopted will keep this enormous multiplication of error from being greatly apparent, except as either end of the Biot formula curve is approached. But throughout the entire range of the observations it is doubtless this multiplication of error in the  $\frac{\partial P}{\partial T}$  that is most often responsible for the variation in the constant.

Many illustrations taken directly from the measurements enforcing the above remarks might be given, but attention will only be called to the case of water. Ramsay and Young's observations of the vapor pressure of water are in beautiful accord ( $0^{\circ}$  to  $230^{\circ}$  C) with the Regnault-Biot formula, whose results they quote. But when this formula is forced past the temperature ( $230^{\circ}$  C) for which it was calculated, an error in the trend ( $\frac{\partial P}{\partial T}$ ) of the formula is at once apparent.<sup>1</sup> This error could neither have been suspected nor provided for, had either set of observations below  $230^{\circ}$  C been used to calculate the formula.

<sup>1</sup> See Phil. Trans. 1892A, p. 112.

In this connection Prof. Young calls my attention to Broch's calculations of the vapor pressure of water, 0° to 100° C. Broch used the formula,

$$P = A_{10} \frac{bt + ct^2 + dt^3 + et^4 + ft^5}{1 + at},$$

and made exceedingly careful and laborious calculations. But unfortunately in obtaining his constants he used Regnault's data from -32° to 100° and the vapor pressures at the lower temperatures were for the most part those of ice, not water. Hence, remarks of Prof. Young, "It is interesting to notice that below 0° his calculated pressures are with trifling exceptions, higher than the vapor pressures of *ice* observed by Regnault—a striking proof, if such were needed, that the vapor pressures of water are really higher than those of ice at the same temperatures. Moreover, Broch makes the vapor pressure of water at 0° = 4.569, whereas the mean of Regnault's actual observations, 12 in number, is 4.608." Again at 100° C, Prof. Young points out that the trend of Broch's curve is certainly wrong, and in proof of this he sends, and kindly permits me to publish, the following calculations upon the vapor pressure of water, made some years ago but never published.

#### Vapor Pressures of Water

Temperatures	From Regnault's curve	From Broch's formula	
100°	760.00	760.00	0.00
120	1489.0	1544.7	55.7
150	3572.0	4244.3	672.3
200	11660.0	31861.0	20201.0
Corrected for latitude, etc. and normal degrees C.			
200°	11660.0	31839.0	20179.0
Preliminary constants before employment of method of least squares			
200°	11660.0	40547.0	28887.0

It surely cannot be necessary to give further illustrations of the fact that the trend of no empirical curve can be trustworthy near its end point.

In conclusion therefore :—

3. Errors of observation occurring in the vapor pressure will exert *per se* little effect upon the constant of formula 2.

4. Errors in the vapor pressure may cause greatly multiplied error in the constant by affecting Biot's formula used for the calculation of the  $\frac{\partial P}{\partial T}$ . This source of error will be greatly more apparent at the end points for which the Biot formula was calculated.

### The Evidence for the Theory

The measurements considered in calculating the constants, of which Table I gives a summary, include thirty-one substances,

TABLE I

Temperature	Ethyl oxide	Di-iso-propyl	Di-iso-butyl	Iso-pentane	Normal pentane	Normal hexane	Normal heptane	Normal octane	Benzene	Hexa-methylene
Mean value	104.4	98.0	88.7	105.4	109.0	101.7	98.4	92.85	109.5	103.6
0°	106.5	97.8	89.1	107.2	111.1	103.6	99.6	97.5	109.3	102.6
10	105.6	...	...	104.8	...	...	...	...	...	...
20	104.4	...	...	104.5	...	...	...	...	...	...
30	103.9	...	...	104.1	107.6	...	...	...	...	...
40	103.5	...	...	104.3	108.5	...	...	...	...	...
50	103.4	98.6	...	104.5	109.3	...	...	...	...	...
60	103.4	98.7	...	104.7	109.5	102.4	...	...	...	...
70	103.5	99.0	...	104.6	109.6	102.7	100.3	...	...	...
80	103.5	98.4	...	105.2	109.7	103.0	99.4	...	107.8	...
90	103.9	98.2	90.4	105.5	109.9	103.0	99.1	...	107.8	105.6
100	103.5	97.8	88.7	105.8	109.9	103.3	99.0	...	108.1	104.8
110	104.7	97.4	87.0	106.0	110.4	103.7	98.9	...	108.3	104.1
120	104.8	97.6	85.8	106.3	111.1	103.6	98.3	91.2	108.6	103.3
130	104.9	97.7	85.0	106.5	111.0	103.5	97.8	91.4	108.8	102.5
140	105.3	97.7	84.9	106.7	110.5	103.2	97.5	91.8	109.1	102.1
150	105.3	97.7	84.6	106.9	110.5	103.1	97.2	92.1	109.4	102.2
160	104.4	97.7	85.7	106.7	110.3	102.5	97.5	92.8	109.5	102.7
170	103.0	97.7	85.7	105.5	110.3	102.4	97.7	92.8	109.8	103.1
180	101.0	98.0	86.2	103.4	109.3	102.6	98.5	92.9	110.0	103.4
190	106.3	98.1	86.8	{ 187.4° 96.6	106.3	102.8	98.9	93.1	110.4	102.9
200	{ 193° 114.5	98.1	87.0	...	{ 197.15° 98.8	102.7	99.2	93.3	110.5	103.1
210	...	97.3	87.3	...	...	102.1	99.7	93.9	110.5	103.5
220	...	94.8	87.9	...	...	101.1	99.7	93.6	110.7	104.2
230	...	{ 225° 92.0	88.6	...	...	98.0	99.8	93.9	111.1	104.6
240	...	...	89.0	...	...	{ 234° 94.2	99.8	93.7	110.6	104.6
250	...	...	89.5	...	...	...	99.3	94.2	110.3	104.9
260	...	...	89.4	...	...	...	96.6	94.6	110.0	104.7
270	...	...	87.6	...	...	...	{ 266.5° 90.8	94.3	110.0	103.4
280	...	...	{ 274° 86.4	...	...	...	...	93.4	107.8	{ 279° 98.1
290	...	...	...	...	...	...	...	91.0	...	...
Critic'l temp.	194°	227.35°	276.8°	187.8°	197.2°	234.8°	266.9°	296.2°	288.5°	279.95°

TABLE I.—(Continued)

Temperature	Fluo- benzene	Chlor- benzene	Brom- benzene	Iodo- benzene	Carbon tetra- chloride	Stannic chloride	Water	Methyl alcohol	Ethyl alcohol	Propyl alcohol	Acetic acid
Mean value	85.7	81.0	56.1	44.2	44.3	26.0	556.0	302.3	240.1	199.2	...
0	84.6	81.6	....	....	43.53	26.20	585.7	304.7	232.8	203.1	....
10	....	....	....	....	....	....	580.1	306.0	235.4	....	...
20	....	....	....	....	....	....	575.2	306.6	237.4	....	81.3
30	....	....	58.74	44.99	....	....	570.7	307.9	239.9	....	83.8
40	....	....	....	....	....	....	566.6	307.4	241.7	....	86.1
50	....	....	....	....	....	....	563.0	308.3	242.4	....	87.8
60	....	....	....	....	....	....	559.9	308.0	243.6	....	90.4
70	....	....	....	....	....	....	556.9	308.1	244.1	....	92.2
80	86.8	....	....	....	....	....	554.5	307.8	244.9	199.9	94.7
90	87.2	....	....	....	43.52	....	552.4	307.1	244.6	199.2	96.4
100	86.9	....	56.93	44.65	43.58	26.45	550.6	306.3	244.8	197.6	98.5
110	86.7	....	....	....	43.58	26.34	549.5	306.0	242.7	196.2	100.7
120	86.3	....	....	....	43.64	26.24	548.6	305.4	242.1	193.6	104.3
130	85.7	79.5	....	....	43.67	26.16	547.8	304.5	241.0	191.3	104.9
140	85.0	80.3	....	....	43.79	26.00	547.6	304.1	241.0	191.1	105.5
150	84.6	81.1	....	....	43.79	25.82	547.3	303.3	241.1	187.8	106.6
160	84.7	80.8	54.09	....	43.83	25.68	547.8	303.1	239.8	185.6	107.9
170	84.7	81.3	54.48	....	43.86	25.46	548.7	302.3	238.2	184.1	111.7
180	84.7	81.2	54.98	....	43.92	25.13	550.4	300.9	236.5	182.7	111.3
190	84.8	81.3	55.21	41.87	44.00	24.84	551.8	300.8	233.3	180.4	113.3
200	84.7	81.3	55.45	42.66	44.16	24.68	553.9	299.3	230.0	178.6	115.4
210	85.1	81.6	55.91	43.06	44.34	24.45	556.4	295.4	226.3	176.6	117.5
220	85.5	81.8	55.87	43.64	44.55	24.20	559.1	287.6	223.0	173.2	119.1
230	85.8	82.3	56.25	43.73	44.76	23.96	563.0	276.5	219.7	168.8	121.5
240	86.2	83.1	56.19	44.03	44.94	23.63	553.6	238.5 <sup>0</sup> 259.4	209.2	164.1	124.1
250	86.6	83.6	56.44	44.38	45.16	23.35	551.0	....	242.5 <sup>0</sup> 197.2	160.2	126.4
260	86.8	84.3	56.92	44.68	44.99	22.96	544.9	....	....	157.0	128.4
270	86.3	84.9	57.15	45.10	44.47	22.47	535.5	....	....	....	130.0
280	84.7	....	....	....	43.90	22.15	....	....	....	....	131.5
290	....	....	....	....	....	....	....	....	....	....	131.2
Critic'l temp.	286.55°	360.7°	397°	448°	283.15°	318.7°	365°	240°	243.6°	263.7°	321.65°

and cover a range of 290° in temperature. The foregoing discussion has shown that errors of observation may often be multiplied and are always compounded in their effect upon this constant. To cover this range of temperature, the number of substances, and the variously compounded errors of observation in vapor pressure, vapor density, and density of the liquid, errors which may be multiplied in the calculation, it has seemed to me reasonable to pass without discussion all variations in the constant less than two percent from the mean values chosen and given at the top of each column. An agreement within two percent of this mean value we therefore consider satisfactory. All values not showing this agreement are in italics.

Excepting values within ten degrees of the critical temperature the eleven substances, ethyl oxide, di-isopropyl, isopentane, normal pentane, normal hexane, normal heptane, normal octane, benzene, hexamethylene, fluo-benzene, and carbon tetrachloride, show out of *two hundred and seventeen* observations only *two* that are not within two percent of the mean value adopted for that particular substance. The two exceptions are normal octane at  $0^{\circ}$  C and ethyl oxide at  $180^{\circ}$  C, and both of these divergences, as well as those occurring within ten degrees of the critical temperature, are, as shown below, easily explained.

In six of the eleven substances above mentioned, the observations allowed the tests of the formula to be carried to within one degree of the critical temperature, and in the case of normal pentane to within  $0.05^{\circ}$  of that point, yet in no case is the divergence greater than ten percent from the mean value adopted for that substance. Nearing the critical temperature an inspection will show that an error in the vapor pressure will be multiplied proportionately some seventy times in the constant if the error likewise affects the  $\frac{\partial P}{\partial T}$  and, as already explained, (p. 395), at the end points of the Biot formula curve these errors do affect, to a considerable degree, the  $\frac{\partial P}{\partial T}$ .

The same explanation will hold for normal octane at  $0^{\circ}$  C.

For ether at  $180^{\circ}$  C reference to the original data shows that the Biot formula adopted differs from the observations sufficiently to account for the divergence, and it is but proper here to add that Prof. Young writes, "Above  $180^{\circ}$  the substance (ether) was heated with methyl salicylate which was not quite satisfactory. In later work quinoline was used."

I think it may be safely said that every error occurring in these eleven substances could be entirely eliminated by changes in Biot's formula, in no case affecting any vapor pressure so much as five-tenths of one percent, and I therefore emphasize the fact that *the only divergences shown from the theory by these eleven substances are not errors of observation, primarily, but of calculation.*

It may be well to mention that of the 217 observations for these eleven substances, 152 are within 1 percent of the average value, and the 63 that are within 2 percent of that value group themselves more largely at those points where errors of calculation and of observation would be the greatest.

These eleven substances, therefore, from 0° C to their critical temperature, show, it seems to the author, as perfect accord with the theory as the method and observations will permit.

Of the other substances, the following observations are not within two percent of the mean values given.

Di-isobutyl, 120° to 190° C, inclusive, shows a divergence amounting at the greatest to five percent from the mean value. This may be caused by an error in the vapor density, because  $P\Delta V$  does not show a maximum value at 2000 mms pressure, and the same value at 5000 to 6000 mms as at 500 to 600 mms, as is the case with similar substances.

Prof. Young has very kindly examined for me his original notes and calculations upon di-isobutyl. The measurements and calculations were abundantly checked, and there would seem to be no chance for unusually large errors. He suggests that if a lower mean value were adopted the errors would be shifted toward the end points of the curve.

The author would here remark that a theory by Crompton to which attention will be called in a following paper, seems to bear out this suggestion, but also points more strongly to the fact that di-isobutyl does not give the results that similar substances would lead one to expect.

Chlor-benzene, 240° to 270° inclusive, may easily be due to the wrong trend  $\left(\frac{\partial P}{\partial T}\right)$  of the Biot formula at this, its end point.

Brom-benzene at 30° C. The error here is due to the Biot formula, as shown by the fact that at 100° C the constant, from a theoretically calculated density, is correct.

At 160° and 170° C the error may be due to the measurement of the vapor density. Prof. Young writes, "The observed volumes of saturated vapor are generally much less accurate at

low temperatures than at high, because, by the method employed, a given error in reading would have much greater influence at the lower temperature." Also regarding brom-benzene Prof. Young says, "After heating in ordinary daylight at  $180^{\circ}$ ,  $190^{\circ}$ ,  $200^{\circ}$ , 'brom-benzene slightly acted on by mercury, small quantity of solid being formed, chiefly in form of minute needle-shaped crystals.' In a second series the brom-benzene was 'carefully shielded from the light, no crystals formed.' The volumes were read in the first series only—the quantity of liquid in the second being small—and the results do not seem to me so satisfactory as with the other substances examined."

Iodo-benzene at  $190^{\circ}$  to  $210^{\circ}$  C, inclusive, may be due to measurement of vapor density. Dr. Young writes, "In the case of iodo-benzene similar crystals (to those with brom-benzene) were found, although the substance was shielded from daylight. All readings had to be taken by gas light and are therefore less accurate than usual."

The tendency towards continually increasing values of the constant with rise in temperature in the case of chlor-benzene, brom-benzene and iodo-benzene, may easily be without significance, for in the first mentioned the tendency is not marked, and in the last two the final values are not far from the probable true values as shown by the results at  $30^{\circ}$  and  $100^{\circ}$  C. On the other hand they may indicate progressive changes commencing within the molecule, and the remarks of Dr. Young above given are significant.

Stannic chloride may be said to be in agreement with the theory from  $0^{\circ}$  C to  $170^{\circ}$  C, but the values from  $100^{\circ}$  to  $280^{\circ}$  continually decrease, and there is little doubt that the cause of the variation is operative from the first. I would call attention to the high specific heat per atom that we find in stannic chloride and the conclusion, based on grounds having nothing to do with the present theory, drawn therefrom by the author,<sup>1</sup> viz: "A high scientific heat per atom indicates that the potential energy of the atoms is being rapidly increased and that the

<sup>1</sup> Jour. Elisha Mitchell Scientific Soc. Vol. 18.



molecule is approaching the point of dissociation."

Prof. Young writes, "Stannic chloride spoils the surface of mercury even at low temperatures and special methods had to be used throughout. The accuracy is certainly not so great as with most of the other substances, but this will not, I think, explain the regular fall in the value of the constant."

Water shows divergence  $0^{\circ}$  to  $30^{\circ}$  C and at  $270^{\circ}$  C. Both may be explained by the multiplication of error through the  $\frac{\partial P}{\partial T}$  at the end points of the Biot formula curve. Ramsay and Young's observations of the vapor pressures at  $230^{\circ}$  to  $270^{\circ}$  are in themselves rather conclusive that the trouble at  $270^{\circ}$  C rests with the Regnault-Biot formula.<sup>1</sup>

See also remarks on page 399. The measurements of Griffiths would indicate that the divergence at the lower temperatures is but partly due to the vapor pressure formula used.

The divergence in ethyl alcohol at  $0^{\circ}$  C is probably caused by the end point of Biot formula used.

Methyl alcohol,  $210^{\circ}$  to  $238.5^{\circ}$  C, ethyl alcohol,  $190^{\circ}$  to  $242.5^{\circ}$  C, and propyl alcohol,  $120^{\circ}$  to  $260^{\circ}$ , evidently should be grouped together. They are associated substances, as was water, and the theory was not expected to hold for associated substances, because the molecules may not be evenly distributed, the molecules are of different kinds, and the number of molecules changes with changing temperature. *The fact that the theory does hold, to a very considerable degree, for these substances also, is significant, and points strongly to the conclusion that the cause of the molecular association in these substances must be the attraction which we are discussing and not some other attraction such as we might denote by the term chemical affinity.* And the fact that these associated substances do not agree even more closely with the theory may be entirely due to the supposition embraced by the formula that the molecules are uniformly distributed throughout the space occupied by them — a supposition probably untrue for associated substances.

<sup>1</sup> See Phil. Trans. 1892A, p. 112.

Bearing in mind the comments above, we conclude that the divergences shown by di-isobutyl, chlor-benzene, brom-benzene, iodo-benzene, and water, all occur at such points and are of such magnitude (none greater than 5.4 percent) that they may easily be due to errors of observation, or the multiplication of such errors by the calculations. Stannic chloride fails to agree with the theory. Water, methyl, ethyl, and propyl alcohols and acetic acid are associated substances to which the theory is not applicable *a priori*, and yet these substances, acetic acid excepted, appear within limits to agree with the theory.

In conclusion, to prevent further misapprehension, I would notice a review by Mr. G. N. Lewis<sup>1</sup> of the former paper on this subject. This paper presents additional evidence in favor of the theory, and it is the intention of the author to extend the work to the ten esters for which measurements have been made by Prof. Young. The "other assumptions of doubtful validity" upon which the present theory is based, referred to in that review, were mentioned in the original paper as they are in this (here they are numbered, however, so that he who runs may read), without attempt at proof. True equations are seldom deduced from wrong assumptions, and if we can establish the truth of the equation the assumptions will probably be admitted by those who now doubt their truth. All of the assumptions made, except possibly the law of attraction assumed, are, we are inclined to believe, regarded favorably by scientists on other grounds. Concerning the statement made in that review that "the author does not point out the simple relations between the densities of vapor and liquid, and the difference in their specific heats, which would be the direct consequence of his equations," we would say that we are of course aware that the equations that we have deduced can be combined with certain other thermodynamical, empirical and rational equations, so as to produce certain relations. (See for instance, equation 13 of this paper, which equation is similar to the relation,  $p = bt - a$ , of Professors Ramsay and Young.) The theory itself here given

<sup>1</sup> Jour. Am. Chem. Soc. 3, 107 (1903).

is capable of further direct and very promising application. The author hopes shortly to complete and publish a paper calling attention to some of these extensions of the theory.

For the measurements used we are indebted almost entirely to the labors of Profs. Ramsay and Young, and of Prof. Young. After months of laborious acquaintance with these measurements we cannot conclude this paper without giving expression to the sincere admiration excited by the accuracy and completeness of the data they have furnished. And we would express a thanks, heartfelt, and echoed doubtless by hundreds of workers elsewhere, for their labors.

We wish further to express our thanks to Prof. Young for some unpublished details of the measurements and for comment upon the work, and we have taken the liberty of making in this paper some extracts from his letters.

### Summary

1. The equation,  $\frac{L - E_1}{\sqrt{d} - \sqrt{D}} = \text{constant}$  was deduced for the purpose of testing the assumption that the attraction between the molecules of any particular substance obeyed the law of gravitation, i. e., varied directly as the product of the masses, inversely as the square of their distance apart, and does not vary with the temperature.

2. Twenty-one substances were examined. Of these, eleven: ethyl oxide, di-isopropyl, isopentane, normal pentane, normal hexane, normal heptane, normal octane, benzene, hexamethylene, fluo-benzene, and carbon tetrachloride were, from  $0^\circ$  C to their critical temperature, making allowance for errors of observation and the multiplication of such errors in the calculation, in reasonably perfect agreement with the deduced equation. The divergences in di-isobutyl, chlor-benzene, brom-benzene, iodo-benzene, and water, all occur at such points and are of such magnitude that they may easily be due to the errors of observation (or the multiplication of such errors in the calculation). Stannic chloride failed to agree with the equation.

3. To the associated substances water, methyl, ethyl, and

propyl alcohols, and acetic acid, the equation was not supposed applicable; but within wide limits the agreement of these substances, acetic acid excepted, is such as to suggest the conclusion that the molecular association with which we are there dealing is caused by the molecular attraction whose law we are considering.

TABLE 2  
Ethyl Oxide

Temperature	Pressure	Density of liquid	Density of vapor	Latent heat	$E_1$	$L - E_1$	$\frac{L - E_1}{\sqrt{d} - \sqrt{D}}$	$\frac{L - E_1}{\sqrt{d} - \sqrt{D}}$
10	184.90	0.7362	0.028270	93.27	7.11	86.16	0.8091	106.5
20	291.78	0.7248	0.001264	90.77	7.33	83.44	0.7901	105.6
30	442.36	0.7135	0.001870	87.90	7.50	80.40	0.7704	104.4
40	647.93	0.7019	0.002677	85.60	7.68	77.92	0.7499	103.9
50	921.18	0.6894	0.003731	83.18	7.82	75.36	0.7283	103.5
60	1276.11	0.6764	0.005079	80.95	7.94	73.01	0.7059	103.4
70	1728.13	0.6658	0.006771	78.84	8.05	70.79	0.6840	103.4
80	2293.91	0.6532	0.008920	76.42	8.07	68.35	0.6603	103.5
90	2991.40	0.6402	0.01155	73.95	8.10	65.85	0.6359	103.5
100	3839.71	0.6250	0.01477	71.39	8.08	63.31	0.6096	103.9
110	4859.01	0.6105	0.01867	68.35	8.02	60.33	0.5830	103.5
120	6070.38	0.5942	0.02349	65.98	7.91	58.07	0.5543	104.7
130	7495.73	0.5764	0.02934	62.63	7.72	54.91	0.5238	104.8
140	9157.42	0.5580	0.03638	59.11	7.49	51.62	0.4919	104.9
150	11078.2	0.5385	0.04488	55.52	7.21	48.31	0.4582	105.5
160	13281.0	0.5179	0.05551	51.18	6.80	44.38	0.4216	105.3
170	15788.1	0.4947	0.06911	45.99	6.25	39.74	0.3805	104.4
180	18622.2	0.4658	0.08731	39.69	5.51	34.18	0.3315	103.0
185	21804.3	0.4268	0.1135	31.58	4.49	27.09	0.2687	101.0
190	23532.4	0.4018	0.1320	26.78	3.82	22.96	0.2287	100.4
192	25355.1	0.3663	0.1620	20.90	2.79	18.11	0.1704	106.3
193	26111.2	0.3448	0.1826	17.10	2.14	14.96	0.1339	111.6
193	26495.0	0.3300	0.2012	13.67	1.64	12.03	0.1051	114.5

TABLE 3  
Di-isopropyl

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{p \Delta v}{T}$ $10^6$	$A$	Latent heat	$E_1$	$L - E_1$	$\bar{v} d - \bar{v} D$	$\frac{L - E_1}{\bar{v} d - \bar{v} D}$
70	76.05	0.6795	0.023840	54.05	1.57468	85.11	6.30	78.81	0.8065	97.81
80	584.1	0.6338	0.002551	73.64	1.06573	78.47	7.26	71.21	0.7224	98.57
90	406.8	0.6243	0.003448	77.49	0.99238	76.90	7.41	69.49	0.7036	98.75
100	1090.3	0.6144	0.004566	81.29	0.92634	75.30	7.54	67.76	0.6842	99.03
110	1444.8	0.6039	0.006006	84.05	0.86685	72.86	7.58	65.28	0.6635	98.39
120	1880.9	0.5931	0.007752	86.90	0.81327	70.67	7.62	63.05	0.6423	98.16
130	2409.7	0.5821	0.009901	89.26	0.76498	68.28	7.61	60.67	0.6203	97.81
140	3043.0	0.5708	0.01250	91.15	0.72144	65.76	7.58	58.18	0.5974	97.38
150	3793.2	0.5589	0.01555	93.18	0.68219	63.57	7.54	56.03	0.5741	97.60
160	4673.0	0.5464	0.01923	94.54	0.64677	61.15	7.47	53.68	0.5496	97.69
170	5697.0	0.5334	0.02358	95.28	0.61479	58.58	7.34	51.24	0.5242	97.75
180	6879.0	0.5197	0.02825	97.46	0.58592	57.10	7.33	49.77	0.4994	99.67
190	8234.0	0.5049	0.03521	94.13	0.55982	52.70	6.92	45.78	0.4685	97.72
200	9781.0	0.4885	0.04292	92.05	0.53623	49.36	6.61	42.75	0.4375	97.71
210	11536.0	0.4705	0.05216	89.06	0.51488	45.86	6.26	39.60	0.4042	97.98
220	13519.0	0.4508	0.06361	84.50	0.49555	41.87	5.81	36.06	0.3676	98.09
230	15752.0	0.4274	0.07831	77.71	0.47803	37.15	5.23	31.92	0.3255	98.07
240	18258.0	0.3988	0.09862	67.28	0.46213	31.09	4.43	26.66	0.2741	97.27
250	19905.0	0.3758	0.1163	57.80	0.45331	26.20	3.76	22.44	0.2335	96.10
260	21062.0	0.3565	0.1321	49.45	0.44770	22.14	3.19	18.95	0.1998	94.84
275	22585.0	0.3198	0.1649	33.04	0.44099	14.57	2.11	12.46	0.1355	91.96

TABLE 4  
Di-isobutyl

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{p \Delta v}{T}$ $10^6$	$A$	Latent heat	$E_1$	$L - E_1$	$\bar{v} d - \bar{v} D$	$\frac{L - E_1}{\bar{v} d - \bar{v} D}$
70	7.11	0.7102	0.044762	40.76	1.98712	80.99	4.75	76.24	0.8560	89.06
80	425.6	0.6328	0.002174	70.82	1.01836	72.12	6.21	65.91	0.7290	90.41
90	581.1	0.6236	0.002967	72.70	0.95256	69.25	6.20	63.05	0.7106	88.73
100	777.9	0.6143	0.003984	74.30	0.89276	66.33	6.17	60.16	0.6916	86.98
110	1022.6	0.6046	0.005236	76.08	0.83846	63.79	6.16	57.63	0.6720	85.76
120	1322.5	0.5945	0.006757	77.98	0.78921	61.54	6.16	55.38	0.6517	84.97
130	1684.9	0.5841	0.008532	80.37	0.74460	59.84	6.19	53.65	0.6316	84.94
140	2118.2	0.5732	0.01072	82.06	0.70425	57.79	6.17	51.62	0.6102	84.59
150	2630.6	0.5620	0.01119	84.30	0.66783	56.30	6.19	50.11	0.589	85.09
160	3231.3	0.5503	0.01610	86.30	0.63500	54.80	6.20	48.60	0.5670	85.71
170	3930.2	0.5383	0.01957	87.61	0.60549	53.05	6.15	46.90	0.5440	86.21
180	4738.0	0.5255	0.02370	88.39	0.57903	51.18	6.08	45.10	0.5197	86.78
190	5666.5	0.5117	0.02874	87.93	0.55539	48.83	5.92	42.91	0.4935	86.96
200	6729.5	0.4970	0.03484	86.80	0.53433	46.38	5.72	40.66	0.4655	87.34
210	7941.0	0.4810	0.04202	84.94	0.51566	43.80	5.48	38.32	0.4358	87.93
220	9319.0	0.4633	0.05094	81.89	0.49918	41.80	5.18	35.70	0.4031	88.56
230	10883.0	0.4434	0.06223	77.10	0.48474	37.37	4.78	32.59	0.3663	88.97
240	12654.0	0.4199	0.07640	70.40	0.47218	33.24	4.28	28.96	0.3237	89.47
250	14660.0	0.3912	0.09699	60.55	0.46135	27.93	3.62	24.31	0.2719	89.41
260	16929.0	0.3482	0.1321	43.21	0.45213	19.54	2.53	17.01	0.1942	87.58
274	18006.0	0.3187	0.1572	31.72	0.44887	14.24	1.85	12.39	0.1434	86.40

TABLE 5  
Isopentane

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{p \Delta v}{T}$ $10^6$	A	Latent heat	$E_1$	$L - E_1$	$\frac{p}{d} - \frac{p'}{d'}$	$\frac{L - E_1}{\frac{p}{d} - \frac{p'}{d'}}$
257.74	0.6392	0.001090	64.43	1.37910	88.86	7.51	81.35	0.7585	107.2	
390.52	0.6295	0.001646	66.96	1.26846	84.93	7.53	77.40	0.7389	104.8	
572.59	0.6196	0.002358	70.88	1.16990	82.91	7.70	75.21	0.7194	104.5	
815.34	0.6092	0.003300	74.45	1.08206	80.55	7.82	72.73	0.6988	104.1	
1131.1	0.5988	0.004480	78.41	1.00375	78.69	7.97	70.72	0.6781	104.3	
1533.2	0.5881	0.005967	82.14	0.93390	76.71	8.09	68.62	0.6564	104.5	
2035.6	0.5769	0.007819	85.55	0.87157	74.56	8.18	66.38	0.6340	104.7	
2653.0	0.5656	0.01011	88.36	0.81591	72.09	8.20	63.89	0.6107	104.6	
3400.8	0.5540	0.01284	91.36	0.76618	70.00	8.24	61.76	0.5871	105.2	
4295.6	0.5413	0.01617	93.54	0.72171	67.51	8.20	59.31	0.5621	105.5	
5354.5	0.5278	0.02022	95.00	0.68194	64.78	8.11	56.67	0.5357	105.8	
6596.1	0.5140	0.02513	95.64	0.64631	61.81	7.95	53.86	0.5081	106.0	
8039.9	0.4991	0.03106	95.42	0.61439	58.62	7.73	50.89	0.4788	106.3	
9706.7	0.4826	0.03831	94.02	0.58574	55.07	7.43	47.64	0.4473	106.5	
11620.0	0.4642	0.04728	91.19	0.56002	51.07	7.03	44.04	0.4127	106.7	
13704.0	0.4445	0.05834	86.92	0.53689	46.67	6.54	40.13	0.3754	106.9	
16285.0	0.4206	0.07289	79.98	0.51605	41.27	5.88	35.39	0.3316	106.7	
19094.0	0.3914	0.09337	68.93	0.49728	34.28	4.95	29.33	0.2778	105.5	
20950.0	0.3694	0.1101	59.90	0.48090	29.17	4.25	24.92	0.2382	104.6	
22622.0	0.3498	0.1258	51.33	0.46803	24.65	3.61	21.04	0.2035	103.4	
23286.0	0.3311	0.1418	42.80	0.45555	20.35	2.99	17.36	0.1703	101.9	
23992.0	0.3142	0.1574	34.86	0.44245	16.47	2.42	14.05	0.1399	100.4	
24550.0	0.3028	0.1676	29.76	0.42793	14.01	2.06	11.95	0.1201	99.5	
24713.0	0.2857	0.1833	22.22	0.40942	10.43	1.54	8.89	0.0905	98.2	
24880.0	0.2761	0.1951	17.21	0.40882	8.07	1.19	6.88	0.0712	96.6	

TABLE 6  
Normal Pentane

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{p \Delta v}{T}$ $10^6$	A	Latent heat	$E_1$	$L - E_1$	$\frac{p}{d} - \frac{p}{d}$	$\frac{L - E_1}{\frac{p}{d} - \frac{p}{d}}$
30	183.40	0.6454	0.097756	64.48	1.44799	93.36	7.51	85.85	0.7723	111.1
40	613.9	0.6165	0.002475	74.84	1.13456	84.91	7.86	77.05	0.7158	107.6
50	865.3	0.6062	0.003390	79.47	1.05221	83.63	8.08	75.55	0.6961	108.5
60	1190.2	0.5987	0.004545	83.91	0.97878	82.13	8.27	73.86	0.6758	109.3
70	1601.8	0.5850	0.006024	87.65	0.91324	80.04	8.38	71.66	0.6544	109.5
80	2114.0	0.5739	0.007868	90.93	0.85466	77.71	8.44	69.27	0.6321	109.6
90	2742.1	0.5624	0.01013	93.86	0.80221	75.30	8.46	66.84	0.6091	109.7
100	3501.5	0.5503	0.01289	96.30	0.75519	72.73	8.45	64.38	0.5850	109.9
110	4409.1	0.5378	0.01629	97.99	0.71297	69.87	8.36	61.51	0.5598	109.9
120	5482.5	0.5248	0.02026	99.62	0.67497	67.24	8.28	58.96	0.5340	110.4
130	6740.5	0.5107	0.02503	100.65	0.64073	64.48	8.15	56.33	0.5068	111.1
140	8203.0	0.4956	0.03106	99.78	0.60979	60.85	7.88	52.97	0.4770	111.0
150	9890.0	0.4797	0.03861	97.26	0.58177	56.58	7.50	49.08	0.4442	110.5
160	11826.0	0.4604	0.04762	94.16	0.55636	52.39	7.09	45.30	0.4097	110.5
170	14032.0	0.4394	0.05910	88.94	0.53323	47.42	6.53	40.89	0.3707	110.3
180	16535.0	0.4161	0.07347	82.13	0.51213	42.06	5.90	36.16	0.3278	110.3
190	19362.0	0.3867	0.09354	71.03	0.49284	35.01	4.99	30.02	0.2746	109.3
200	21225.0	0.3643	0.1109	61.14	0.48205	29.47	4.24	25.23	0.2337	108.0
210	22540.0	0.3445	0.1269	51.95	0.47516	24.68	3.57	21.11	0.1985	106.3
220	23566.0	0.3253	0.1441	42.50	0.47014	19.08	2.90	17.08	0.1634	104.5
230	24271.0	0.3055	0.1609	33.54	0.46685	15.66	2.28	13.38	0.1303	102.7
240	24629.0	0.2915	0.1745	26.55	0.46524	12.35	1.70	10.55	0.1042	101.2
250	24810.0	0.2809	0.1842	21.78	0.46443	10.12	1.48	8.64	0.0859	100.6
260	24901.0	0.2640	0.2004	14.12	0.46363	6.55	0.96	5.59	0.0563	99.3
270	25027.0	0.2560	0.2090	10.34	0.46347	4.79	0.70	4.09	0.0415	98.5
27.15	25045.0	0.2472	0.2167	6.71	0.46339	3.11	0.45	2.66	0.0269	98.3

TABLE 7  
Normal Hexane

Temperature °	Pressure	Density of liquid	Density of vapor	$\frac{\rho \Delta v}{T}$ $10^6$	$\alpha$	Latent heat	$E_1$	$L - E_1$	$\frac{\rho \Delta v - \rho D}{\rho \Delta v}$	$\frac{L - E_1}{\rho \Delta v - \rho D}$
60	44.92	0.6770	0.02268	54.05	1.68307	90.98	6.30	84.68	0.8171	103.6
70	567.62	0.6221	0.00249	75.68	1.06787	80.82	7.23	73.59	0.7182	102.4
80	784.80	0.6122	0.00337	79.51	0.99598	79.19	7.38	71.81	0.6992	102.7
90	1062.0	0.6022	0.00446	83.31	0.93083	77.55	7.51	70.04	0.6799	103.0
100	1409.0	0.5918	0.00585	86.61	0.87180	75.51	7.60	67.91	0.6594	103.0
110	1838.0	0.5814	0.00752	90.00	0.81835	73.65	7.68	65.97	0.6387	103.3
120	2358.0	0.5703	0.00952	93.18	0.76998	71.75	7.74	64.01	0.6174	103.7
130	2982.0	0.5588	0.01200	95.54	0.72623	69.38	7.74	61.64	0.5947	103.6
140	3723.0	0.5467	0.01502	97.24	0.68669	66.78	7.68	59.10	0.5710	103.5
150	4593.0	0.5343	0.01862	98.25	0.65098	63.96	7.57	56.39	0.5464	103.2
160	5506.0	0.5207	0.02299	98.64	0.61874	61.03	7.42	53.61	0.5201	103.1
170	6778.0	0.5063	0.02833	97.73	0.58968	57.63	7.18	50.45	0.4921	102.5
180	8123.0	0.4913	0.03472	96.44	0.56352	54.34	6.93	47.41	0.4629	102.4
190	9659.0	0.4751	0.04228	94.31	0.53998	50.93	6.63	44.30	0.4319	102.6
200	11407.0	0.4570	0.05155	90.89	0.51883	47.16	6.25	40.91	0.3981	102.8
210	13385.0	0.4365	0.06329	85.52	0.49986	43.75	5.75	37.00	0.3601	102.7
220	15619.0	0.4124	0.07900	77.23	0.48289	37.29	5.09	32.20	0.3152	102.1
230	18133.0	0.3809	0.1011	64.93	0.46773	30.37	4.19	26.18	0.2590	101.1
240	19788.0	0.3557	0.1203	53.97	0.45943	24.79	3.46	21.33	0.2148	99.3
250	20957.0	0.3329	0.1404	43.43	0.45421	19.73	2.75	16.98	0.1732	98.0
260	21870.0	0.3040	0.1658	30.32	0.45045	13.66	1.90	11.76	0.1230	95.6
270	22181.0	0.2883	0.1807	23.24	0.44923	10.44	1.46	8.98	0.0953	94.2

TABLE 8  
Normal Heptane

Temperature °	Pressure	Density of liquid	Density of vapor	$\frac{\rho \Delta v}{T}$ $10^6$	$\alpha$	Latent heat	$E_1$	$L - E_1$	$\frac{\rho \Delta v - \rho D}{\rho \Delta v}$	$\frac{L - E_1}{\rho \Delta v - \rho D}$
70	11.45	0.7005	0.06725	46.46	1.93423	99.86	5.42	84.44	0.8474	99.6
80	302.77	0.6402	0.001435	72.17	1.13368	81.84	6.70	75.14	0.7491	100.3
90	427.10	0.6311	0.001996	75.22	1.08722	79.52	6.78	72.74	0.7319	99.4
100	588.74	0.6218	0.002703	78.66	0.98784	77.70	6.90	70.80	0.7142	99.1
110	794.93	0.6124	0.003584	82.13	0.92493	75.96	7.01	68.95	0.6962	99.0
120	1053.3	0.6027	0.004692	85.33	0.86789	74.06	7.09	66.97	0.6773	98.6
130	1372.1	0.5926	0.006068	87.95	0.81624	71.79	7.12	64.67	0.6576	98.3
140	1759.9	0.5821	0.007752	90.27	0.76948	69.46	7.13	62.33	0.6371	97.8
150	2226.1	0.5711	0.009775	92.39	0.72719	67.19	7.12	60.07	0.6159	97.5
160	2780.4	0.5581	0.01508	94.08	0.68898	64.81	7.08	57.13	0.5939	97.2
170	3433.3	0.5481	0.01848	95.87	0.65447	62.74	7.05	55.69	0.5713	97.5
180	4196.0	0.5359	0.02422	97.02	0.62337	60.48	6.97	53.51	0.5479	97.7
190	5080.9	0.5232	0.03217	98.30	0.59536	58.52	6.92	51.62	0.5238	98.5
200	6101.3	0.5096	0.04304	98.30	0.57017	56.05	6.76	49.29	0.4982	98.9
210	7271.8	0.4952	0.05394	97.14	0.54757	53.17	6.54	46.63	0.4703	99.2
220	8608.6	0.4793	0.06805	95.15	0.52730	50.17	6.27	43.90	0.4405	99.7
230	10130.0	0.4616	0.08621	91.25	0.50919	46.46	5.89	40.57	0.4071	99.8
240	11857.0	0.4414	0.10602	85.81	0.49305	42.31	5.43	36.88	0.3698	99.8
250	13811.0	0.4177	0.1277	78.24	0.47860	37.25	4.85	32.60	0.3268	99.8
260	16020.0	0.3877	0.16061	67.05	0.46598	31.25	4.08	27.17	0.2735	99.0
270	18511.0	0.3477	0.2087	48.15	0.45475	21.90	2.88	19.02	0.1909	98.0
280	20595.0	0.3166	0.2538	35.15	0.45466	15.84	2.08	13.76	0.1458	94.4
290	22150.0	0.2807	0.3007	23.73	0.44869	10.65	1.40	9.25	0.1001	92.4
300	23300.0	0.2519	0.3695	18.97	0.44821	8.50	1.12	7.38	0.0813	90.8

TABLE 9  
Normal Octane

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{P \Delta v}{T}$ 10 <sup>6</sup>	A	Latent heat	$E_1$	$L - E_1$	$\bar{v} - \bar{v}^D$	$\frac{L - E_1}{\bar{v} - \bar{v}^D}$
0°	2.90	0.7185	0.01942	40.77	2.1942	89.46	4.75	84.71	0.8688	97.50)
120	649.3	0.6168	0.003300	76.91	0.91369	70.27	6.24	64.03	0.7023	91.17
130	859.4	0.6071	0.00429	80.16	0.85906	68.86	6.33	62.53	0.6842	91.39
140	1114.5	0.5973	0.005464	83.47	0.80944	67.56	6.43	61.13	0.6661	91.77
150	1426.9	0.5875	0.006897	86.50	0.76440	66.12	6.51	59.61	0.6471	92.12
160	1802.4	0.5772	0.008584	89.59	0.72354	64.82	6.58	58.24	0.6278	92.77
170	2249.0	0.5667	0.01065	91.74	0.68649	62.98	6.59	56.39	0.6075	92.83
180	2775.4	0.5556	0.01314	93.41	0.65293	60.99	6.56	54.43	0.5861	92.87
190	3390.7	0.5441	0.01608	94.82	0.62252	59.03	6.52	52.51	0.5640	93.10
200	4105.0	0.5317	0.01957	95.54	0.59501	56.87	6.43	50.44	0.5406	93.30
210	4928.9	0.5189	0.02364	96.17	0.57015	54.83	6.34	48.49	0.5166	93.86
220	5874.6	0.5053	0.02874	95.00	0.54769	52.03	6.13	45.90	0.4902	93.63
230	6955.0	0.4901	0.03484	93.41	0.52743	49.27	5.91	43.36	0.4618	93.90
240	8184.5	0.4732	0.04237	90.29	0.50918	45.97	5.60	40.37	0.4307	93.73
250	9578.8	0.4554	0.05118	86.87	0.49276	42.80	5.29	37.51	0.3981	94.22
260	11156.0	0.4364	0.06223	81.87	0.47802	39.14	4.89	34.25	0.3622	94.56
270	12937.0	0.4123	0.07710	73.96	0.46480	34.33	4.33	30.05	0.3186	94.32
280	14942.0	0.3818	0.09833	62.38	0.45298	28.26	3.59	24.67	0.2639	93.40
290	17198.0	0.3365	0.1346	43.18	0.44243	19.10	2.44	16.66	0.1831	91.00

TABLE 10  
Benzene

Temperature	Pressure	Density of liquid	Density of vapor	Latent heat	$E_1$	$L - E_1$	$\bar{v} - \bar{v}^D$	$\frac{L - E_1}{\bar{v} - \bar{v}^D}$
80°	26.54	0.9001	0.001215	107.05	6.95	100.10	0.9160	109.3
90	753.62	0.8145	0.002722	94.40	8.78	85.62	0.7943	107.8
100	1016.1	0.8041	0.003570	92.76	9.02	83.74	0.7771	107.8
110	1344.3	0.7927	0.004690	91.05	9.07	81.98	0.7581	108.1
120	1748.2	0.7809	0.006035	89.20	9.15	80.05	0.7388	108.3
130	2238.1	0.7692	0.007634	87.36	9.24	78.12	0.7194	108.6
140	2824.9	0.7568	0.009515	85.43	9.33	76.10	0.6994	108.8
150	3520.0	0.7440	0.01174	83.48	9.39	74.09	0.6789	109.1
160	4334.8	0.7310	0.01436	81.35	9.42	71.93	0.6577	109.4
170	5281.9	0.7185	0.01734	79.20	9.46	69.74	0.6368	109.5
180	6374.1	0.7043	0.02087	76.90	9.43	67.47	0.6144	109.8
190	7625.2	0.6906	0.02487	74.53	9.41	65.12	0.5920	110.0
200	9049.4	0.6758	0.02977	71.93	9.25	62.68	0.5676	110.4
210	10663.0	0.6605	0.03546	69.01	9.06	59.95	0.5424	110.5
220	12482.0	0.6432	0.04207	65.80	8.83	56.97	0.5154	110.5
230	14526.0	0.6255	0.05015	62.32	8.48	53.84	0.4864	110.7
240	16815.0	0.6065	0.06024	58.49	8.00	50.49	0.4545	111.1
250	19369.0	0.5851	0.07138	54.21	7.58	46.63	0.4216	110.6
260	22214.0	0.5609	0.08454	49.40	7.01	42.39	0.3841	110.3
270	25376.0	0.5328	0.10318	43.76	6.27	37.49	0.3407	110.0
280	28845.0	0.4984	0.1287	36.97	5.30	31.67	0.2890	110.0
290	32772.0	0.4514	0.1660	27.43	3.98	23.45	0.2175	107.8



TABLE II  
Hexamethylene

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{P \Delta v}{T}$ 10 <sup>6</sup>	A	Latent heat	$E_1$	$L - E_1$	$\frac{P \Delta v}{T} - \frac{P \Delta v}{T}$	$\frac{L - E_1}{\frac{P \Delta v}{T} - \frac{P \Delta v}{T}}$
90	27.85	0.7967	0.021374	55.34	1.73860	96.22	6.45	89.77	0.8754	102.6
100	992.34	0.7106	0.003759	95.32	0.90396	86.17	8.36	77.81	0.7369	105.6
110	1306.8	0.7003	0.004902	98.77	0.84748	83.71	8.43	75.28	0.7181	104.8
120	1691.0	0.6898	0.006289	102.03	0.79610	81.23	8.48	72.75	0.6990	104.1
130	2155.4	0.6791	0.007968	105.01	0.74938	78.69	8.51	70.18	0.6793	103.3
140	2709.1	0.6680	0.01000	107.52	0.70695	76.01	8.49	67.52	0.6588	102.5
150	3362.0	0.6565	0.01238	110.11	0.66844	73.60	8.49	65.11	0.6378	102.1
160	4124.5	0.6448	0.01508	112.90	0.63349	71.52	8.49	63.03	0.6168	102.2
170	5007.3	0.6325	0.01818	115.78	0.60183	69.68	8.51	61.17	0.5955	102.7
180	6021.9	0.6200	0.02183	117.93	0.57314	67.99	8.47	59.52	0.5732	103.1
190	7199.9	0.6067	0.02625	119.05	0.54721	65.15	8.36	56.79	0.5494	103.4
200	8494.5	0.5926	0.03140	118.62	0.52377	62.13	8.15	53.98	0.5245	102.9
210	9980.2	0.5780	0.03738	118.11	0.50263	59.37	7.95	51.42	0.4986	103.1
220	11651.0	0.5626	0.04437	116.84	0.48358	56.50	7.70	48.80	0.4715	103.5
230	13526.0	0.5456	0.05249	114.82	0.46645	53.56	7.41	46.15	0.4427	104.2
240	15622.0	0.5271	0.06250	110.81	0.45107	49.98	7.01	42.97	0.4109	104.6
250	17961.0	0.5063	0.07496	104.65	0.43732	45.76	6.49	39.27	0.3754	104.6
260	20565.0	0.4820	0.09058	96.52	0.42504	41.02	5.87	35.15	0.3350	104.9
270	23461.0	0.4533	0.1111	84.91	0.41409	35.16	5.07	30.09	0.2874	104.7
277	26860.0	0.4125	0.1433	66.08	0.40441	26.72	3.87	22.85	0.2210	103.4
279	29146.0	0.3642	0.1855	42.31	0.39829	16.85	2.45	14.40	0.1438	100.1
279	29878.0	0.3393	0.2105	29.69	0.39664	11.78	1.71	10.07	0.1026	98.1

TABLE 12  
Fluo-benzene

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{P \Delta v}{T}$ 10 <sup>6</sup>	A	Latent heat	$E_1$	$L - E_1$	$\frac{P \Delta v}{T} - \frac{P \Delta v}{T}$	$\frac{L - E_1}{\frac{P \Delta v}{T} - \frac{P \Delta v}{T}}$
80	20.92	1.0465	0.021179	48.43	1.80422	87.39	5.65	81.74	0.9662	84.60
90	645.98	0.9496	0.002885	78.79	1.01612	80.06	7.10	72.96	0.8405	86.80
100	879.73	0.9366	0.003831	83.03	0.95108	78.97	7.28	71.69	0.8219	87.22
110	1174.9	0.9233	0.005040	86.46	0.89163	77.09	7.38	69.71	0.8023	86.86
120	1541.3	0.9096	0.006515	89.97	0.83731	75.33	7.48	67.85	0.7821	86.75
130	1989.2	0.8955	0.008333	92.94	0.78772	73.21	7.53	65.68	0.7611	86.29
140	2529.5	0.8811	0.01055	95.49	0.74249	70.90	7.54	63.36	0.7394	85.69
150	3173.0	0.8665	0.01321	97.67	0.70128	68.50	7.53	60.97	0.7170	85.03
160	3931.4	0.8519	0.01634	99.78	0.66379	66.26	7.51	58.75	0.6942	84.63
170	4816.7	0.8363	0.01992	102.23	0.62970	64.37	7.51	56.86	0.6711	84.73
180	5841.6	0.8203	0.02413	104.08	0.59678	62.32	7.48	54.84	0.6471	84.74
190	7018.9	0.8037	0.02911	105.28	0.57076	60.09	7.40	52.69	0.6221	84.70
200	8363.5	0.7857	0.03496	105.84	0.54542	57.83	7.28	50.55	0.5958	84.85
210	9800.5	0.7671	0.04184	105.71	0.52257	55.24	7.11	48.13	0.5683	84.66
220	11617.0	0.7480	0.04968	105.43	0.50202	52.93	6.95	45.98	0.5401	85.09
230	13561.0	0.7265	0.05907	103.97	0.48356	50.28	6.71	43.57	0.5095	85.51
240	15745.0	0.7036	0.07037	101.30	0.46708	47.32	6.41	40.91	0.4766	85.84
250	18198.0	0.6789	0.08403	97.32	0.45241	44.03	6.04	38.00	0.4409	86.19
260	20924.0	0.6504	0.1008	91.70	0.43941	40.29	5.58	34.71	0.4010	86.58
270	23977.0	0.6163	0.1226	83.50	0.42796	35.74	4.99	30.75	0.3541	86.85
277	27384.0	0.5739	0.1535	70.96	0.41796	29.66	4.16	25.50	0.2956	86.26
280	31182.0	0.5133	0.2034	51.20	0.40928	20.95	2.95	18.00	0.2126	84.69

TABLE 13  
Chlor-benzene

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{p \Delta v}{T}$ $10^6$	A	Latent heat	$E_1$	$L - E_1$	$\frac{p \Delta v}{T} - \frac{p \Delta v}{T}$	$\frac{L - E_1}{p \Delta v - \frac{p \Delta v}{T}}$
130	2.56	1.1278	0.041689	41.36	2.12075	87.72	4.82	82.90	1.0152	81.65
140	720.03	0.9836	0.003409	84.81	0.86978	73.77	6.70	67.07	0.8440	79.46
150	938.84	0.9723	0.004316	89.45	0.82021	73.37	6.89	66.48	0.8279	80.30
160	1206.0	0.9599	0.005394	94.06	0.77491	72.89	7.08	65.81	0.8111	81.13
170	1528.3	0.9480	0.006761	97.14	0.73356	71.26	7.14	64.12	0.7933	80.83
180	1912.8	0.9354	0.008312	101.00	0.69585	70.28	7.26	63.02	0.7754	81.27
190	2367.2	0.9224	0.01020	103.97	0.66150	68.77	7.31	61.46	0.7566	81.24
200	2899.4	0.9091	0.01240	106.80	0.63023	67.31	7.34	59.97	0.7373	81.34
210	3518.3	0.8955	0.01500	109.08	0.60183	65.65	7.34	58.31	0.7173	81.29
220	4233.0	0.8802	0.01798	111.36	0.57607	64.15	7.34	56.81	0.6964	81.58
230	5053.8	0.8672	0.02145	113.27	0.55273	62.60	7.31	55.29	0.6757	81.82
240	5991.8	0.8518	0.02544	114.92	0.53164	61.10	7.27	53.83	0.6538	82.31
250	7059.6	0.8356	0.03000	116.36	0.51263	59.65	7.22	52.43	0.6312	83.06
260	8270.5	0.8196	0.0354	116.92	0.49553	57.93	7.12	50.81	0.6075	83.64
270	9639.8	0.8016	0.0417	116.74	0.48021	56.06	6.97	49.09	0.5821	84.33
270	11185.0	0.7834	0.0492	115.64	0.46653	53.95	6.78	47.17	0.5554	84.93

TABLE 14  
Brom-benzene

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{p \Delta v}{T}$ $10^6$	A	Latent heat	$E_1$	$L - E_1$	$\frac{p \Delta v}{T} - \frac{p \Delta v}{T}$	$\frac{L - E_1}{p \Delta v - \frac{p \Delta v}{T}}$
100	5.67	1.4815	0.044702	36.54	1.87985	68.68	3.84	64.84	1.1039	58.74
110	141.23	1.3864	0.009519	55.30	1.13159	62.58	4.72	57.86	1.0166	56.93
120	840.81	1.2994	0.005255	68.99	0.79276	54.69	5.07	49.62	0.9174	54.09
130	1071.6	1.2647	0.005533	72.06	0.75220	54.21	5.18	49.03	0.9000	54.48
140	1349.3	1.2697	0.008071	75.24	0.71501	53.80	5.29	48.51	0.8822	54.98
150	1679.9	1.2534	0.009911	77.88	0.68085	53.02	5.35	47.67	0.8634	55.21
160	2070.1	1.2385	0.01205	80.49	0.64942	52.27	5.42	46.85	0.8447	55.45
170	2527.0	1.2210	0.01450	83.18	0.62046	51.61	5.48	46.13	0.8250	55.91
180	3057.8	1.2037	0.01750	84.90	0.59370	50.41	5.48	44.93	0.8041	55.87
190	3670.2	1.1876	0.02080	87.21	0.56895	49.62	5.52	44.10	0.7840	56.25
200	4372.5	1.1689	0.02482	88.45	0.54600	48.29	5.49	42.80	0.7617	56.19
210	5173.0	1.1510	0.02927	90.06	0.52467	47.25	5.48	41.77	0.7398	56.44
220	6080.8	1.1310	0.03427	91.72	0.50483	46.30	5.48	40.82	0.7171	56.92
230	7104.8	1.1099	0.04016	92.59	0.48632	45.03	5.43	39.60	0.6929	57.15

TABLE 15  
Iodo-benzene

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{p \Delta v}{T}$ $10^6$	A	Latent heat	$E_1$	$L - E_1$	$\frac{p \Delta v}{T} - \frac{p \Delta v}{T}$	$\frac{L - E_1}{p \Delta v - \frac{p \Delta v}{T}}$
100	1.48	1.8149	0.041595	28.11	2.0170	56.70	2.95	53.75	1.1946	44.99
110	50.23	1.7079	0.04400	42.57	1.2612	53.68	3.62	50.06	1.1193	44.65
120	787.88	1.5627	0.006020	60.37	0.74721	45.11	4.14	40.97	0.9785	41.87
130	990.60	1.5470	0.007215	63.77	0.71100	45.34	4.28	41.06	0.9624	42.66
140	1232.0	1.5316	0.008889	66.51	0.67797	45.10	4.38	40.72	0.9456	43.06
150	1517.1	1.5115	0.01070	69.37	0.64792	44.94	4.47	40.47	0.9272	43.64
160	1851.5	1.4941	0.01266	71.25	0.62066	44.22	4.50	39.72	0.9083	43.73
170	2241.2	1.4764	0.01552	73.32	0.59602	43.70	4.54	39.16	0.8893	44.03
180	2693.2	1.4581	0.01849	75.20	0.57374	43.15	4.56	38.59	0.8695	44.38
190	3214.9	1.4384	0.02199	76.71	0.55395	42.50	4.57	37.93	0.8486	44.68
200	3815.0	1.4172	0.02605	78.06	0.53614	41.85	4.56	37.29	0.8268	45.10

TABLE 16  
Carbon Tetrachloride

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{p \Delta v}{T}$ $10^4$	A	Latent heat	$E_1$	$L - E_1$	$p^*d - p^*D$	$\frac{L - E_1}{p^*d - p^*D}$
100 °	33.08	1.6327	0.02984	30.27	1.7135	51.87	3.52	48.35	1.1107	43.53
100	1117.0	1.4554	0.007974	50.56	0.89103	45.05	4.43	40.62	0.9334	43.52
110	1464.8	1.4343	0.01026	52.89	0.83590	44.20	4.52	39.68	0.9105	43.58
120	1869.4	1.4124	0.01304	54.99	0.78563	43.21	4.57	38.64	0.8866	43.58
130	2400.8	1.3902	0.01634	57.08	0.73997	42.24	4.61	37.63	0.8623	43.64
140	3009.1	1.3680	0.02024	59.05	0.69855	41.25	4.67	36.58	0.8376	43.67
150	3725.1	1.3450	0.02481	60.92	0.66093	40.26	4.70	35.56	0.8121	43.79
160	4559.6	1.3215	0.03021	62.37	0.62679	39.09	4.67	34.42	0.7860	43.79
170	5524.6	1.2982	0.03680	63.70	0.59581	37.95	4.67	33.28	0.7592	43.83
180	6631.9	1.2734	0.04386	64.66	0.56775	36.71	4.64	32.07	0.7312	43.86
190	7894.8	1.2470	0.05249	65.27	0.54234	35.40	4.57	30.83	0.7020	43.92
200	9326.7	1.2192	0.06250	65.55	0.51927	34.04	4.52	29.52	0.6714	44.00
210	10943.0	1.1888	0.07418	65.42	0.49841	32.61	4.39	28.22	0.6391	44.16
220	12759.0	1.1566	0.08787	64.83	0.47957	31.09	4.26	26.83	0.6051	44.34
230	14793.0	1.1227	0.1040	63.67	0.46257	29.45	4.10	25.35	0.5690	44.55
240	17066.0	1.0857	0.1232	61.80	0.44722	27.64	3.91	23.73	0.5301	44.76
250	19596.0	1.0444	0.1464	59.01	0.43338	25.56	3.65	21.91	0.4875	44.94
260	22409.0	0.9980	0.1754	55.08	0.42093	23.19	3.34	19.85	0.4395	45.16
270	25532.0	0.9409	0.2146	48.99	0.40973	20.07	2.92	17.15	0.3812	44.99
280	28992.0	0.8666	0.2710	39.92	0.39971	15.96	2.34	13.62	0.3063	44.47
280	32825.0	0.7634	0.3597	26.68	0.39071	10.43	1.53	8.90	0.2027	43.90

TABLE 17  
Stannic Chloride

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{p \Delta v}{T}$ $10^4$	A	Latent heat	$E_1$	$L - E_1$	$p^*d - p^*D$	$\frac{L - E_1}{p^*d - p^*D}$
100 °	5.88	2.2789	0.08996	17.84	1.98373	35.38	2.08	33.30	1.2711	26.26
110	496.5	2.0186	0.005704	31.89	0.98455	31.40	2.72	28.68	1.0845	26.45
120	672.7	1.9916	0.007634	33.24	0.92427	30.72	2.76	27.96	1.0612	26.34
130	891.4	1.9639	0.009940	34.54	0.86900	30.02	2.80	27.22	1.0373	26.24
140	1162.0	1.9357	0.01276	35.82	0.81835	29.32	2.83	26.49	1.0126	26.16
150	1491.0	1.9073	0.01616	36.95	0.77193	28.52	2.85	25.67	0.9873	26.00
160	1888.0	1.8772	0.02024	37.93	0.72941	27.67	2.85	24.82	0.9611	25.82
170	2359.0	1.8481	0.02506	38.92	0.69047	26.86	2.86	24.00	0.9345	25.68
180	2914.0	1.8182	0.03077	39.63	0.65482	25.95	2.85	23.10	0.9071	25.46
190	3561.0	1.7873	0.03759	40.00	0.62219	24.89	2.81	22.08	0.8786	25.13
200	4309.0	1.7556	0.04545	40.30	0.59234	23.87	2.77	21.10	0.8494	24.84
210	5168.0	1.7224	0.05450	40.65	0.56504	22.97	2.74	20.23	0.8195	24.68
220	6147.0	1.6886	0.06502	40.64	0.54009	21.95	2.68	19.27	0.7882	24.45
230	7257.0	1.6488	0.07728	40.39	0.51730	20.89	2.61	18.28	0.7554	24.20
240	8509.0	1.6090	0.09149	39.80	0.49648	19.86	2.52	17.28	0.7212	23.96
250	9915.0	1.5667	0.10833	38.96	0.47748	18.60	2.42	16.18	0.6847	23.63
260	11488.0	1.5221	0.12830	37.79	0.46016	17.39	2.30	15.09	0.6463	23.35
270	13242.0	1.4747	0.1520	36.07	0.44438	16.03	2.15	13.88	0.6045	22.96
280	15190.0	1.4210	0.1812	33.82	0.43001	14.54	1.98	12.56	0.5578	22.47
280	17351.0	1.3628	0.2160	31.38	0.41694	13.08	1.81	11.27	0.5087	22.15

TABLE 18  
Water

Temperature	Pressure	Density of liquid	Density of vapor	Latent heat	$E_1$	$L - E_1$	$\bar{v}d - \bar{v}'d$	$\frac{L - E_1}{\bar{v}d - \bar{v}'d}$
10	4.569	0.9999	0.044737	606.5	30.7	575.8	0.9831	585.7
20	9.140	0.9997	0.069200	599.5	31.6	567.9	0.9790	580.1
30	17.363	0.9982	0.041699	592.6	32.5	560.1	0.9737	575.2
40	31.510	0.9957	0.042995	585.7	33.5	552.2	0.9675	570.7
50	54.865	0.9923	0.045071	578.6	34.4	544.2	0.9604	566.6
60	91.978	0.9881	0.048278	571.6	35.4	536.2	0.9524	563.0
70	148.885	0.9833	0.051303	564.7	36.3	528.4	0.9437	559.9
80	233.308	0.9779	0.051989	557.6	37.3	520.3	0.9342	556.9
90	354.873	0.9719	0.052052	550.6	38.2	512.4	0.9240	554.5
100	525.468	0.9655	0.05273	543.5	39.1	504.4	0.9131	552.4
110	766.000	0.9586	0.05031	536.5	40.1	496.4	0.9015	550.6
120	1075.37	0.9512	0.048389	529.4	40.8	488.6	0.8892	549.5
130	1484.0	0.9441	0.046138	522.3	41.4	480.9	0.8766	548.6
140	2019.0	0.9365	0.044522	515.1	42.1	473.0	0.8634	547.8
150	2694.0	0.9283	0.042000	508.0	42.8	465.2	0.8495	547.6
160	3568.0	0.9193	0.0402592	500.7	43.7	457.0	0.8349	547.3
170	4652.0	0.9095	0.038313	493.6	44.5	449.1	0.8198	547.8
180	5937.0	0.8989	0.04181	486.2	45.0	441.2	0.8040	548.7
190	7487.0	0.8881	0.045216	479.0	45.4	433.6	0.7878	550.4
200	9403.0	0.8766	0.048439	471.6	46.1	425.5	0.7711	551.8
210	11625.0	0.8646	0.0507855	464.3	46.7	417.6	0.7539	553.9
220	14240.0	0.8523	0.052506	456.8	47.1	409.7	0.7363	556.4
230	17365.0	0.8393	0.05140	449.4	47.8	401.6	0.7182	559.1
240	20936.0	0.8256	0.051369	441.9	48.4	393.5	0.6989	563.0
250	25019.0	0.8117	0.051632	433.8	47.8	376.0	0.6791	553.6
260	29734.0	0.7980	0.051944	410.4	47.5	362.9	0.6586	551.0
270	35059.0	0.7840	0.052315	394.0	46.8	347.2	0.6371	544.9
280	41101.0	0.7701	0.052766	374.5	45.6	328.9	0.6142	535.5

TABLE 19  
Methyl Alcohol

Temperature	Pressure	Density of liquid	Density of vapor	Latent heat	$E_1$	$L - E_1$	$\bar{v}d - \bar{v}'d$	$\frac{L - E_1}{\bar{v}d - \bar{v}'d}$
10	29.6	0.8101	0.045620	289.17	16.77	272.40	0.8939	304.7
20	54.7	0.8000	0.049960	287.36	17.48	269.88	0.8819	306.0
30	96.0	0.7905	0.041695	284.54	18.03	266.51	0.8692	306.6
40	160.0	0.7830	0.042772	282.07	18.37	263.70	0.8565	307.9
50	260.5	0.7745	0.044394	277.78	18.87	258.91	0.8423	307.4
60	406.0	0.7650	0.046739	274.14	19.16	254.98	0.8269	308.3
70	625.0	0.7555	0.041006	269.41	19.75	249.66	0.8106	308.0
80	926.6	0.7460	0.041465	264.51	20.10	244.41	0.7933	308.1
90	1341.0	0.7355	0.042084	258.96	20.43	238.53	0.7750	307.8
100	1897.0	0.7250	0.042907	252.76	20.70	232.06	0.7557	307.1
110	2621.0	0.7140	0.043984	246.01	20.82	225.19	0.7353	306.3
120	3561.0	0.7020	0.045376	239.27	20.92	218.35	0.7135	306.0
130	4751.0	0.6900	0.047142	232.00	20.95	211.05	0.6911	305.4
140	6242.0	0.6770	0.049379	224.07	20.88	203.19	0.6672	304.5
150	8071.0	0.6640	0.051216	216.12	20.74	195.38	0.6424	304.1
160	10336.0	0.6495	0.051562	206.13	20.55	185.58	0.6160	301.3
170	13027.0	0.6340	0.051994	198.34	20.15	178.19	0.5879	303.1
180	16292.0	0.6160	0.052526	188.25	19.70	168.55	0.5575	302.3
190	20089.0	0.5980	0.053186	177.16	19.01	158.15	0.5255	300.9
200	24615.0	0.5770	0.054010	165.64	18.18	147.46	0.4902	300.8
210	29787.0	0.5530	0.055075	151.84	16.97	134.87	0.4506	299.3
220	35770.0	0.5255	0.056521	134.78	15.29	119.49	0.4045	295.4
230	42573.0	0.4900	0.058635	112.53	12.92	99.61	0.3464	287.6
240	46297.0	0.4675	0.1003	99.50	11.54	87.96	0.3114	282.4
250	50414.0	0.4410	0.1187	84.47	9.87	74.60	0.2697	276.5
260	52202.0	0.4295	0.1277	77.73	9.14	68.59	0.2509	273.4
270	53939.0	0.4145	0.1381	70.15	8.29	61.86	0.2287	270.5
280	55624.0	0.3955	0.1505	61.66	7.27	54.39	0.2020	269.2
290	57576.0	0.3795	0.1681	50.22	5.96	44.26	0.1663	266.1
300	58329.0	0.3635	0.1789	44.23	5.27	38.96	0.1502	259.4

TABLE 20  
Ethyl Alcohol

Temperature °	Pressure	Density of liquid	Density of vapor	Latent heat	$R_1$	$L - R_1$	$\bar{p} - \bar{p}'$	$\frac{L - R_1}{\bar{p} - \bar{p}'}$
10	12.24	0.8062	0.043300	220.9	11.7	209.2	0.8086	232.81
20	23.73	0.7979	0.046207	221.2	12.2	209.0	0.8079	235.4
30	43.97	0.7894	0.051110	220.6	12.6	208.0	0.8061	237.4
40	78.11	0.7810	0.051910	220.1	13.0	207.1	0.8053	239.9
50	133.42	0.7722	0.053150	218.7	13.4	205.3	0.8049	241.7
60	219.82	0.7633	0.055060	216.0	13.8	202.2	0.8042	242.4
70	350.21	0.7541	0.057900	213.4	14.2	199.2	0.8178	243.6
80	540.01	0.7446	0.061190	209.9	14.5	195.4	0.8004	244.1
90	811.81	0.7348	0.064740	206.4	14.8	191.6	0.7821	244.9
100	1186.5	0.7251	0.068500	201.6	15.0	186.6	0.7627	244.6
110	1692.3	0.7157	0.073510	197.1	15.3	181.8	0.7425	244.8
120	2359.8	0.7057	0.079860	190.3	15.4	174.9	0.7209	242.7
130	3221.0	0.6955	0.086580	184.2	15.4	168.8	0.6973	242.1
140	4318.7	0.6859	0.093770	177.6	15.5	162.1	0.6727	241.0
150	5686.6	0.6761	0.01152	171.1	15.4	155.7	0.6461	241.0
160	7368.7	0.6669	0.01488	164.7	15.4	149.3	0.6198	241.1
170	9409.9	0.6582	0.01916	156.9	15.2	141.7	0.5910	239.8
180	11858.0	0.6505	0.02446	148.4	14.8	133.6	0.5608	238.2
190	14764.0	0.5984	0.03115	139.2	14.3	124.9	0.5281	236.5
200	18184.0	0.5782	0.03970	126.4	13.6	114.8	0.4919	233.3
210	22182.0	0.5568	0.05080	116.6	12.6	104.0	0.4523	230.0
220	26826.0	0.5391	0.06550	101.2	11.4	91.8	0.4057	226.3
230	32196.0	0.4958	0.08540	88.2	9.9	78.3	0.3511	223.0
240	38380.0	0.4550	0.1135	70.6	8.1	62.5	0.2849	219.7
250	45519.0	0.3825	0.1715	40.3	4.7	35.6	0.1703	209.2
260	54288.0	0.3703	0.1835	25.0	4.0	31.0	0.1499	206.8
270	64706.0	0.3546	0.1990	16.4	3.3	25.1	0.1239	202.6
280	77463.0	0.3419	0.2164	12.1	2.6	19.5	0.0989	197.2

TABLE 21  
Propyl Alcohol

Temperature °	Pressure	Density of liquid	Density of vapor	Latent heat	$R_1$	$L - R_1$	$\bar{p} - \bar{p}'$	$\frac{L - R_1}{\bar{p} - \bar{p}'}$
80	3.44	0.8193	0.041212	194.4	9.0	185.4	0.9127	203.1
90	376.0	0.7520	0.00104	173.0	11.4	161.5	0.8081	199.9
100	574.0	0.7425	0.00156	169.0	11.7	157.3	0.7895	199.2
110	842.5	0.7325	0.00226	164.0	11.8	152.2	0.7702	197.6
120	1206.0	0.7220	0.00320	159.0	11.9	147.1	0.7497	196.2
130	1683.0	0.7110	0.00443	153.0	12.0	141.0	0.7284	193.6
140	2293.0	0.6995	0.00605	147.0	12.0	135.0	0.7055	191.3
150	3074.0	0.6875	0.00805	142.4	12.0	130.4	0.6822	191.1
160	4052.0	0.6740	0.01060	135.3	11.9	123.4	0.6571	187.8
170	5264.0	0.6600	0.01380	129.0	11.9	117.1	0.6308	185.6
180	6695.0	0.6450	0.01770	122.8	11.7	111.1	0.6034	184.1
190	8343.0	0.6285	0.0225	116.3	11.4	104.9	0.5743	182.7
200	10466.0	0.6110	0.0282	109.6	11.4	98.2	0.5442	180.4
210	12801.0	0.5920	0.0353	102.2	10.8	91.4	0.5117	178.6
220	15575.0	0.5715	0.0442	94.5	10.4	84.1	0.4763	176.6
230	18679.0	0.5485	0.0556	85.3	9.6	75.7	0.4369	173.2
240	22154.0	0.5230	0.0704	75.0	8.7	66.3	0.3927	168.8
250	26194.0	0.4920	0.0904	63.4	7.5	55.9	0.3406	164.1
260	30745.0	0.4525	0.1180	50.6	6.2	44.4	0.2772	160.2
270	36103.0	0.3905	0.1610	33.5	4.2	29.3	0.1868	157.0

TABLE 22  
Acetic Acid

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{P \Delta V}{T}$ $10^6$	A	Latent heat	$E_1$	$L - E_1$	$\frac{P}{T} - \frac{P'}{T'}$	$\frac{L - E_1}{\frac{P}{T} - \frac{P'}{T'}}$
20	11.73	1.0491	0.07645	....	....	84.05	4.88	79.17	0.9737	81.3
30	20.61	1.0392	0.081204	....	....	85.88	5.19	80.69	0.9627	83.8
40	34.77	1.0284	0.082012	....	....	87.02	5.17	81.85	0.9507	86.1
50	56.56	1.0175	0.083100	....	....	88.14	5.81	82.33	0.9381	87.8
60	88.04	1.0060	0.084621	....	....	89.60	6.12	83.57	0.9247	90.4
70	136.0	0.9948	0.086729	....	....	90.43	6.43	84.00	0.9107	92.2
80	202.3	0.9835	0.089588	....	....	91.50	6.71	84.88	0.8959	94.7
90	293.7	0.9718	0.091338	....	....	91.88	6.98	84.90	0.8803	96.4
100	417.1	0.9599	0.091833	....	....	92.32	7.23	85.09	0.8641	98.5
110	580.8	0.9483	0.092468	....	....	92.79	7.47	85.32	0.8474	100.7
120	804.0	0.9362	0.093271	96.24	0.98068	94.38	7.79	85.59	0.8298	104.3
130	1083.0	0.9225	0.094275	101.60	0.91636	93.11	8.02	85.09	0.8112	104.9
140	1431.0	0.9091	0.095516	106.51	0.86227	91.83	8.21	83.62	0.7920	105.5
150	1863.0	0.8961	0.097032	111.21	0.81598	90.74	8.37	82.37	0.7725	106.6
160	2392.0	0.8818	0.098873	115.57	0.77567	89.63	8.49	81.14	0.7519	107.9
170	3034.0	0.8688	0.01084	122.49	0.74002	90.65	8.80	81.85	0.7329	111.7
180	3809.0	0.8554	0.01370	123.89	0.70799	87.71	8.70	79.01	0.7100	111.3
190	4735.0	0.8417	0.01681	127.79	0.67685	86.75	8.78	77.97	0.6880	113.3
200	5836.0	0.8264	0.02052	131.21	0.65202	85.55	8.83	76.72	0.6646	115.4
210	7134.0	0.8117	0.02488	134.23	0.62709	84.17	8.85	75.32	0.6409	117.5
220	8655.0	0.7943	0.03021	135.87	0.60374	82.02	8.77	73.25	0.6147	119.1
230	10426.0	0.7758	0.03626	137.82	0.58171	80.16	8.72	71.44	0.5879	121.5
240	12475.0	0.7576	0.04327	139.43	0.56084	78.18	8.64	69.54	0.5605	124.1
250	14832.0	0.7358	0.05163	139.69	0.54097	75.55	8.50	67.05	0.5304	126.4
260	17527.0	0.7138	0.06165	138.42	0.52199	72.26	8.26	64.00	0.4986	128.4
270	20590.0	0.6896	0.07364	135.64	0.50381	68.33	7.95	60.37	0.4643	130.0
280	24055.0	0.6596	0.08834	130.33	0.48637	63.39	7.50	55.89	0.4251	131.5
290	27951.0	0.6337	0.1073	121.83	0.46963	57.21	6.89	50.32	0.3837	131.2
300	32312.0	0.5956	0.1331	107.95	0.45350	48.95	6.00	42.95	0.3308	129.8
310	37168.0	0.5423	0.1718	86.23	0.43798	37.77	4.71	33.06	0.2595	127.4
320	42550.0	0.4615	0.2591	42.64	0.42301	18.04	2.29	15.75	0.1353	116.4

## THE DISSOCIATION OF LEAD NITRATE

BY J. LIVINGSTON R. MORGAN.

In a recent paper with the above title,<sup>1</sup> Baekeland has given the vapor pressure of solid lead nitrate at different temperatures; but for some reason has made no application of the possible theoretical relations to his results. As the application of some of these shows much concerning the equilibrium, which is lost by his purely qualitative treatment, and as Mr. Baekeland has evidently no intention of considering the question further, the results of such application are presented in this paper.

When heated, lead nitrate dissociates according to the following scheme :



Baekeland's results are as follows :

TABLE I.  
Dissociation pressure of  $\text{Pb}(\text{NO}_3)_2$

Temperatures. °C.	Pressures in millimeters
223	6.2
230	6.9
250	11.8
274	32.6
296	78.4
357	514.0
400	800.0 <sup>2</sup>
448	1180.0

In addition to these vapor pressures of the pure lead nitrate, he also gives the vapor pressure in the presence of an excess of oxygen and an excess of nitrogen peroxide. The

<sup>1</sup> Jour. Am. Chem. Soc. 26, 391-399 (1904).

<sup>2</sup> Interpolated from Mr. Baekeland's curve, l. c. 396.

average values only of these are given in Tables II and III in order to reduce the experimental error to as low a value as possible.

TABLE II.

Vapor pressure of  $\text{Pb}(\text{NO}_3)_2$  in presence of an excess of oxygen (in mm.)  $t = 357^\circ \text{C}$ .

Excess of free oxygen	Total pressure of gases	Dissociation pressure of $\text{Pb}(\text{NO}_3)_2$
425	587	162
467	586	119

TABLE III.

Vapor pressure of  $\text{Pb}(\text{NO}_3)_2$  in presence of an excess of nitrogen peroxide (in mm.)  $t = 357^\circ \text{C}$ .

Excess of free nitrogen peroxide	Total pressure of gases	Dissociation pressure of $\text{Pb}(\text{NO}_3)_2$
635	785	150

### Application of the Law of Mass Action

Applying first the law of mass action to the reaction



it is apparent that

$$\pi_1 K = \sqrt{p_1} p_2^2 \pi_2,$$

where  $K$  is the dissociation constant for the temperature in question,  $\pi_1$  and  $\pi_2$  the active masses of the solids,  $\text{Pb}(\text{NO}_3)_2$  and  $\text{PbO}$ ,  $p_1$  the partial pressure of the oxygen, and  $p_2$  that of the nitrogen peroxide. Omitting the active masses of the solids as constant, we should have then at any one temperature,

$$\sqrt{p_1} p_2^2 = \text{constant.} \quad \text{I.}$$

At  $357^\circ \text{C}$ , from Table I, we find the total pressure of the gases from pure  $\text{Pb}(\text{NO}_3)_2$  equal to 0.514 meter of mercury. Of this one-fifth must be oxygen and four-fifths nitrogen peroxide; hence  $p_1 = 0.103$ ,  $p_2 = 0.412$ , and



$$\sqrt{p_1 p_2} = \sqrt{0.103(0.412)} = \text{constant} = 0.062.$$

This constant value should also be given when one of the products of dissociation is previously present. From Table III we find that in presence of 0.635 (meter of mercury) of nitrogen peroxide we have 0.150 of gases from the  $\text{Pb}(\text{NO}_3)_2$ . Of this the oxygen is one-fifth  $(0.150) = 0.030$ , and the nitrogen peroxide is four-fifths  $(0.150) = 0.120$ , which when applied in the equation gives,

$$\sqrt{0.03(0.120 + 0.635)} = 0.098.$$

That this high value is due to a slight experimental error is shown by the fact that a change of pressure of 10 mm in the nitrogen peroxide does not change the pressure of the gases from the  $\text{Pb}(\text{NO}_3)_2$ . We may assume then that an excess of the nitrogen peroxide keeps the reaction in its normal form. When an excess of oxygen is present, on the other hand, the reaction apparently becomes abnormal. From Table II, by aid of the law of mass action, we have

$$\sqrt{0.032} + 425(0.128)^2 = 0.011$$

and

$$\sqrt{0.024} + 467(0.096)^2 = 0.0091.$$

It has already been observed that under certain conditions a basic nitrate of lead  $3\text{PbO} \cdot 2\text{N}_2\text{O}_5$ , or  $(\text{PbO})_3\text{N}_2\text{O}_5$ , can be formed which has a very much smaller vapor pressure than the normal salt. From these results it would seem that an excess of oxygen favors the formation of this from the normal salt, and causes a different reaction to take place, and consequently gives a different constant.

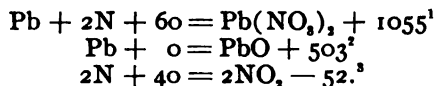
#### Application of van 't Hoff Equation

The values in Table I can be used in van 't Hoff's equation to find the heat of dissociation of lead nitrate. We have

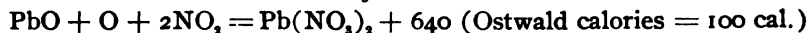
$$q = \frac{i \times R \times 2.302 \times T_1 \times T_2 \left( \log \frac{P_2}{T_2} - \log \frac{P_1}{T_1} \right)}{T_2 - T_1} \quad \text{II}$$

where  $i$  is the number of gram-molecules of gas formed from one

of the original substance (2.5 in this case);  $R$  the molecular gas constant, i. e., Ostwald 0.02 cal; 2.302, the reciprocal of the modulus of the system of logarithms;  $T$ , the lower absolute temperature, for which the dissociation pressure is  $P_1$ ;  $T_2$ , the higher, corresponding to  $P_2$ , and  $q$  the heat of dissociation for the mean temperature, viz.  $\frac{T_1 + T_2}{2}$ . Before using this equation, however, we must consider just what value should be found. The heat of formation of  $\text{Pb}(\text{NO}_3)_2$  has been determined by experiment only from the elements. To get the value from  $\text{PbO}$ ,  $\text{O}$  and  $2\text{NO}_2$ , it is necessary to know the heat value of  $\text{PbO}$  and  $2\text{NO}_2$ . We find



From these equations we get as the experimental value of the heat of formation of  $\text{Pb}(\text{NO}_3)_2$



This value, it is to be remembered, is under atmospheric pressure. The  $q$ , found by aid of equation II, however, is for the case that no external work is done by the gases as they form, or done on them when they disappear. To get the above result of 604 Ostwald calories in terms of no external work, it is necessary then to subtract from it the heat value of the work done by the atmosphere during the decrease in volume. If this is done, the negative value will correspond to the  $q$  in equation II. For the loss of every gram-molecule of gas the work, in terms of heat, is  $RT$  Ostwald calories, where  $R = 0.02$ . In the case of lead nitrate we have a loss in volume equal to that of 2.5 gram-molecules of gas; i. e.,  $\frac{1}{2}\text{O}_2 + 2\text{NO}_2$ , so that the amount to be subtracted from the 604 in order to compare it with  $q$  (equation II) is  $2.5 \times 0.02 T$ , where  $T$  is the average temperature, the  $\frac{T_1 + T_2}{2}$  of equation II.

<sup>1</sup> Ostwald's Lehrbuch, II, 341.

<sup>2</sup> Ostwald. l. c. 348.

<sup>3</sup> Berthelot. Comptes rendus, 90, 779 (1880).

Applying the values given in Table I to equation II and comparing them with the experimental values, we get the following results:

TABLE IV.  
Heats of dissociation of  $\text{Pb}(\text{NO}_3)_2$ .

Temperatures (absolute)			Heat of dissociation in Ostwald calories	
$T_1$	$T_2$	Average	Equation II.	Observed
523	547	535	579	578
547	569	558	593	576
569	630	599	523	574
630	673	646	147 <sup>1</sup>	572
630	721	675	172	571

The equation (II) holds perfectly for the first result where the difference in temperature and pressure is small. The other results, with the exception of the second, are all low, which may be due to experimental errors.

#### Résumé

The application of the law of mass action to Baekeland's vapor pressures of lead nitrate, shows the constant product  $1/\overline{p_{\text{O}}}(p_{\text{NO}_2})^2$  to have the value 0.062 at 357° C.

The addition of  $\text{NO}_2$  in excess shows the presence still of the normal scheme of dissociation.

The addition of oxygen evidently favors the formation of other salts, richer in oxygen, and the scheme of dissociation is changed.

The application of van't Hoff's law gives for the case of low temperature the value of the heat of dissociation equal to the negative value of the heat of formation under like conditions, i. e., 578 Ostwald calories.

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<sup>1</sup> This value in Table I was interpolated from the curve given in the paper, so great stress may not be laid upon it.

# THE CONSTITUTION OF THE COPPER-ZINC ALLOYS

BY E. S. SHEPHERD

Many attempts have been made to determine whether or not copper and zinc unite in definite proportions with the formation of the so-called definite compounds. From electromotive force measurements, Laurie<sup>1</sup> and Herschkowitsch<sup>2</sup> have fixed on  $\text{CuZn}_2$  as a definite compound, while Charpy<sup>3</sup> was led to the same conclusion by microscopic observations. Baker<sup>4</sup> determined the heat of formation of these alloys and obtained a maximum at  $\text{CuZn}_2$ , with a possible minimum at  $\text{CuZn}$ .

In 1897, Roberts-Austen<sup>5</sup> published the freezing-point curve for these alloys, and since that time no further results have appeared. From this curve, as published, we see that there must be at least five different solid phases possible in the system copper-zinc. From microscopic examinations we were led to suspect the existence of one more quadruple point, which was overlooked by Roberts-Austen. This one  $Nz$  (Diagram 1) was actually recorded by the above investigator, but it did not extend over a sufficient range to attract his attention. We also found that the line  $Dd'$  is a curved line dropping as would be indicated by the points registered below  $Dd'$  in the diagram. We are not able to verify his observations as to the existence of the line  $e'e''$ . We made repeated records of the cooling curves of alloys ranging in composition between 50 and 75 percent Cu, without finding such a heat change in any case. These records were made with the scale of the pyrometer magnified so that the range  $400^\circ$ – $550^\circ$  covered the full breadth of the photographic plate, i. e., 28 cm.

We have also made tests by annealing ingots above and

<sup>1</sup> Laurie. Jour. Chem. Soc. 53, 104 (1888).

<sup>2</sup> Herschkowitsch. Zeit. Phys. Chem. 27, 123 (1898).

<sup>3</sup> Charpy. Bull. Soc. d'Encour. (5) 2, 384 (1897). Contributions à l'étude des alliages, Paris, 1901, I.

<sup>4</sup> Baker. Proc. Roy. Soc. London, 68, 9 (1901).

<sup>5</sup> Roberts-Austen. Fourth Report of the Alloys Research Committee.

below  $470^{\circ}$  and quenching. Such ingots show not the slightest change of structure. The temperatures chosen were  $400^{\circ}$  and  $500^{\circ}$ . It follows therefore that the curve  $e'e''$  is due to experimental error, possibly to the sticking of the pyrometer record. This hypothesis is supported by the fact that this change  $e'e''$  appears for concentrations ranging from 75.4 to 16 percent copper, frequently jumping a curve or two only to reappear in the next. Then too, it is often absent in one or two records for the same composition. The quadruple point  $Nn$  is made necessary from a microscopic examination. Alloys containing from 45 to about 63 percent of copper consist of homo-

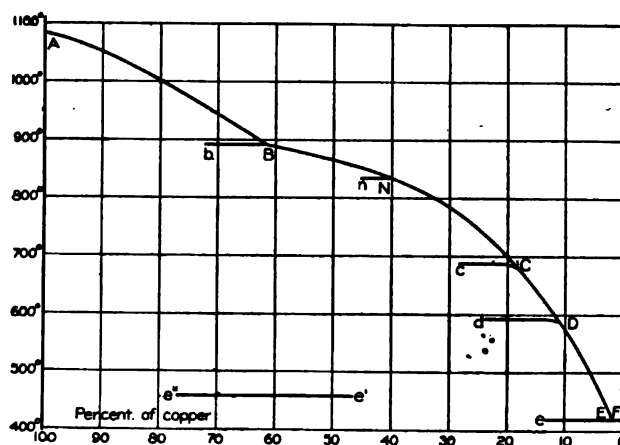


Diagram 1

geneous reddish-yellow crystals above 45 percent copper. Below 45 percent a new kind of crystal appears, mixed with decreasing amounts of the red ones. These crystals are a brilliant silvery color, and at 40 percent copper constitute the entire mass of the ingot, the red crystals having entirely disappeared. Since we cannot have two different kinds of crystals appearing on the same branch of the freezing-point curve there is, of necessity, a quadruple point somewhere between 19 and 60 percent of copper.

By casting these brasses in water, and thus fixing the constituents as they first appear, and from the examination of annealed specimens, we found that the two phases occurring at this quadruple point first appear at about 45 percent Cu and extend

to very nearly 40 percent Cu. By pyrometric determinations we found also, that a second halt in the cooling curve existed over the same range of concentrations.

The freezing-point curve, or liquidus, for this series of alloys, consists of six branches. Consequently there can exist six different solid phases, one in equilibrium with each branch of the curve. It now remains to show what is the nature of these phases.

It may simplify matters to say at the beginning that there are no "definite compounds" between copper and zinc. The six phases are all solid solutions, whose compositions are indicated in Diagram 2, and may be summarized as follows:

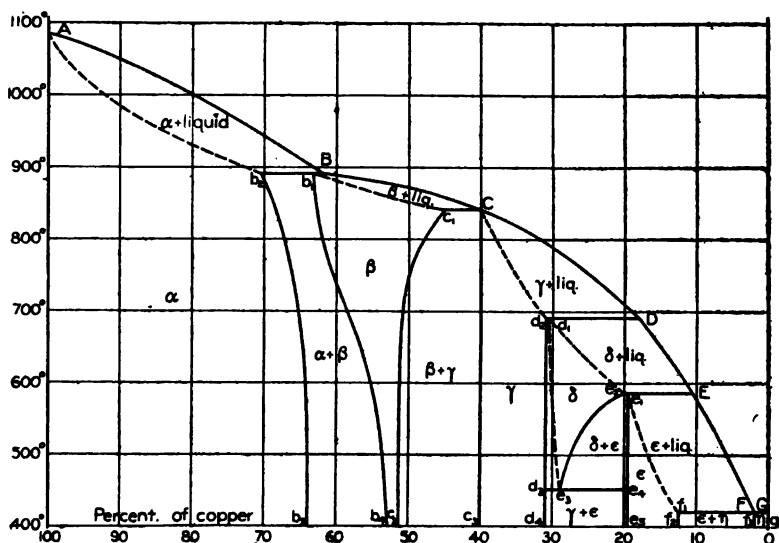


Diagram 2

Liquidus	Solidus	Limits of composition of crystals at 400°
100-63 % Cu	$\alpha$ 71-100 % Cu	64-100 % Cu
63-40 " "	$\beta$ 45- 64 " "	51- 53.5 " "
40-19 " "	$\gamma$ 31- 40 " "	31- 40 " "
19-12 " "	$\delta$ 23- 30 " "	Instable
12- 2 " "	$\epsilon$ 13- 19 " "	13- 19 " "
2- 0 " "	$\eta$ 0- 2.5 " "	0- 2.5 " "

The  $\alpha$ -crystals (Diagram 2), which vary in color from clear yellow to copper-red, occupy the field between the copper axis and the lines  $Ab_2b_3$ . In this region the ingots consist of homogeneous  $\alpha$ -crystals. The exact direction of the solidus  $Ab_2$  is not known. From some experiments, made by Roberts-Austen, in which the mother-liquor was squeezed out and the crystals analyzed, it would seem that the line is a curved one, and of about the shape indicated. From concentrations along the lower part of AB there will first separate  $\alpha$ -crystals, which will later break down along the line  $Bb_2$  with the formation of  $\beta$ -crystals. Within the field  $b_1b_2b_3b_4$  lies a region for mixed  $\alpha$ - and  $\beta$ -crystals. The 63.8 percent alloys shows mixed  $\alpha$  and  $\beta$ , Fig. 7, when annealed at  $700^\circ$  or  $800^\circ$ , but is homogeneous  $\alpha$  at  $400^\circ$ . The 66.3 percent alloy shows only  $\alpha$  when annealed at  $700^\circ$ , but shows mixed  $\alpha$  and  $\beta$  when annealed at  $800^\circ$ . These data give the direction of the line  $b_2b_3$ . The boundary  $b_1b_4$  is determined in a similar way.

Mixed  $\alpha$  and  $\beta$  look like Fig. 7. This photograph has been etched to bring out the masses of  $\beta$  between the lobes of  $\alpha$ .

Along Bc the phase  $\beta$  is stable. It is a solid solution whose composition varies markedly with the temperature. Its limits are indicated by the lines  $b_1b_4$  and  $c_1c_2$ . At higher temperatures the ingots are red in color and homogeneous. At lower temperatures this homogeneous solid solution breaks down with the formation (exudation) of  $\alpha$ -crystals along the line  $b_1b_4$  and of  $\gamma$ -crystals along the line  $c_1c_2$ . The curves  $b_1b_4$  and  $c_1c_2$  do not meet (at least not at ordinary temperatures) for if they did there would be a quadruple point for  $\alpha$ ,  $\beta$ ,  $\gamma$  and vapor. The  $\beta$ -phase would then disappear on annealing below this temperature, with the formation of  $\alpha$  and  $\gamma$ . Numerous experiments have shown, however, that  $\alpha$  and  $\gamma$  are never present in the same ingot. Between 51 and 53 percent of copper the annealed ingots consist entirely of the red  $\beta$ -crystals. At 54 percent Cu the ingots consist of mixed red and yellow  $\alpha$ - and  $\beta$ -crystals; and below 51 percent Cu they consist of red and white  $\beta$ - and  $\gamma$ -crystals. By annealed we mean (unless the temperature is stated) that the alloys have been held at  $350^\circ$ – $400^\circ$  for three weeks. The curve

$b_1b_4$  has not been followed pyrometrically owing to the slowness of the change. It can easily be determined by annealing and quenching the alloys at suitable temperatures. Thus the 58.5 percent alloy is homogeneous when annealed at  $720^\circ$  and quenched. It becomes inhomogeneous, showing both  $\alpha$ - and  $\beta$ -crystals, if annealed at  $685^\circ$  and quenched. The 56.9 percent alloy shows *only*  $\beta$ -crystals when quenched from  $685^\circ$ , but it shows both  $\alpha$ - and  $\beta$ -crystals when quenched after annealing at  $640^\circ$ .

Similarly, the 50 percent alloy is inhomogeneous, showing  $\gamma$ - and  $\beta$ -crystals when annealed at  $640^\circ$ ; but is homogeneous when quenched from  $750^\circ$ . The 52 percent copper alloy differs from all of these by being homogeneous at all temperatures above  $400^\circ$  and probably at lower temperatures. At least, it has not been observed to break down during six months at ordinary temperatures, or three days at  $300^\circ$ .

In the red color of the  $\beta$ -crystals we have the explanation of the red color of the 40–60 percent Cu brasses. Those in the field  $b_1b_2b_3b_4$  being mixed red and yellow, crystals are less red when annealed than those in the field  $Cc_1c_2c_3$ , which are mixed red and white  $\beta$ - and  $\gamma$ -crystals.

Along the branch CD of the liquidus the silver-white brittle crystals  $\gamma$  are in equilibrium with the melt. The composition of these crystals lies between 31 and 40 percent Cu. The field for pure  $\gamma$  is bounded by the lines  $Cc_3d_4d_2$ . It has not been shown directly that  $Cc_3$  and  $d_4d_2$  are exactly vertical lines. It seems probable that they curve slightly. From the experiments made both sides of these compositions, the variation cannot be greater than three percent over the temperature range given. For  $d_4d_2$  the variation cannot be greater than two percent. Regardless of heat treatment these alloys present the same homogeneous structure. Their marked brittleness and bright silvery color are in such contrast to other crystals of this series that it is not surprising that they should have been mistaken for a compound  $CuZn_2$ .

Along DE, the phase  $\delta$  crystallizes from the melt. This phase is instable at lower temperatures, breaking up along the



line  $e_2e_3$  into  $\delta$  and  $\epsilon$  and along  $d_1e_3$  into  $\delta$  and  $\gamma$ . So marked is this change of  $\epsilon\delta$  into  $\epsilon$  that it can be followed pyrometrically over to 29 percent Cu. The exact position of  $d_1e_3$  is unknown, and it is shown as a dotted line, but it lies between 29 and 31 percent, leaving a field  $d_1d_2d_3e_3$  for mixed  $\gamma$  and  $\delta$ . It is possible that lines  $d_2d_3$  and  $d_1e_3$  coincide. The line  $e_2e_3$  necessitates the existence of the invariant system  $\gamma$ ,  $\delta$ ,  $\epsilon$  and vapor which exists along the line  $e_3e_4$ . The course of the curves  $e_2e_3$  and  $e_3e_4$  was checked by cooling curves run on one kilogram of the alloy. Below  $e_3e_4$  the alloy consists of mixed  $\gamma$  and  $\epsilon$ . The  $\epsilon$ -crystals are a solid solution whose concentrations vary from 13–20 percent Cu. They are stable along the branch EF of the liquidus. Alloys containing from 2.5–14 percent copper consist when solid of a mixture of  $\epsilon$ - and  $\eta$ -crystals, the  $\eta$ -crystals being stable along the liquidus FG. The region  $Ff_3g_1G$  is the region for pure  $\eta$ -crystals. It is well known that the addition of copper to zinc raises the freezing-point.

There is evidently a relation between the curves  $b_2b_3$  and  $b_1b_4$ , and the properties of "burnt" and overheated brass. The few samples of burnt brass submitted showed the mixed  $\alpha$ - and  $\beta$ -crystals. If they had not been annealed at such a high temperature they would have been homogeneous  $\alpha$ . But it seems better to leave the discussion of "burnt" brass until the mechanical properties are studied experimentally.

## II. The Micro-structure of Brasses

Charpy<sup>1</sup> has done a considerable amount of work on the physical properties of brasses and has published a series of photomicrographs, but he confined himself to the commercially useful alloys, and no systematic examination of brasses has thus far appeared.

As might be expected from the equilibrium diagram, there is little difference in appearance between the cast and annealed brasses above 70 percent Cu. For both the cast and annealed, the color changes with increasing zinc content from a reddish to

<sup>1</sup> Charpy. loc. cit.

a clear yellow. When etched, these brasses show broad leaf-like crystals, which are difficult to photograph because the figure is one depending on the direction in which the light strikes the crystal. By vertical light the markings are much less pronounced. The cast ingots when deeply etched show a dendritic structure similar to the  $\alpha$ -crystals of bronze, but this is due to the crystals being richer in copper when they first crystallize, and consequently the zinc-rich edges are dissolved first, leaving a net-work effect. In annealed specimens where equilibrium has been reached, diffusion has rendered the crystals uniform in composition and the net-work effect is not found on etching. This is shown in photographs 1-4. All are magnified  $\times 40$  using oblique light. It will be seen that the cast specimens show the dendritic structure, while the annealed specimens are pitted irregularly by the etching,

At 63.8 percent the cast alloy shows the  $\alpha$ -crystals, Fig. 5. The same section magnified  $\times 200$  is shown by Fig. 6. When annealed at  $800^\circ$  and quenched, a mixture of  $\alpha$ - and  $\beta$ -crystals is seen, Fig. 7. In this case the  $\beta$ -crystals are the narrow masses running through a ground mass of large rounded lobes of the  $\alpha$ -crystals. Annealed at  $400^\circ$  the 63.8 percent alloy shows homogeneous  $\alpha$ -crystals. This dendritic structure persists in cast brasses down to 63 percent. Over the range  $b_1b_4$  we have  $\alpha$ - and  $\beta$ -crystals in equilibrium with the melt, the liquid phase disappearing as the temperature falls below that of the quadruple point. At temperatures and concentrations above the line  $b_1b_3$  the alloys consist of mixed  $\alpha$  and  $\beta$ . Below  $b_1b_3$  they are homogeneous  $\alpha$ .

From concentrations lying along the liquidus BC the  $\beta$ -crystals are the first to separate, Fig. 8. They are a bright coppery color and occupy nearly the whole ingot at 62 percent Cu. Annealing at or below  $700^\circ$  causes the exudation of masses of  $\alpha$ , giving structures like Figs. 11 and 12.

Ingots annealed and quenched from points in the field  $b_1b_2b_3b_4$  show the structure of Fig. 9. This structure is so different from Figs. 11 and 12, that we were at first inclined to attribute it to the presence of a new phase lying between the

phases  $\alpha$  and  $\beta$ . We finally discovered that the difference between the structure of Figs. 9 and 11 was due to the method of formation. A structure like Fig. 9 results when the crystals of Fig. 6 break down, forming mixed  $\alpha$  and  $\beta$ ; the original orientation of the  $\alpha$ -crystals is partially retained and the fine-grained structure of Fig. 9 results. If the  $\alpha$ -crystals are exuded from the  $\beta$  solid solution as the mass cools, a structure like Figs. 11 and 12 results. This same structure appears for mixed  $\beta$ - and  $\gamma$ -crystals. In Fig. 7 we have a similar case. This ingot, originally dendritic  $\alpha$ , had been annealed at  $400^\circ$  until it was homogeneous  $\alpha$ . It was then brought to a temperature of  $800^\circ$  and annealed. As the temperature rose above the line  $b_2b_3$ , the alloy has passed into the field for mixed  $\alpha$  and  $\beta$ . Consequently  $\beta$ -crystals would be exuded from the homogeneous mass of  $\alpha$  and we should find a structure similar to Figs. 11 and 12. Such is seen to be the case. If an alloy of such composition be cooled from the melt to  $800^\circ$ , annealed at that temperature and quenched, the structure similar to Fig. 9 results. This is sufficient reason for believing that the change of structure is not due to a change of phase. A careful pyrometric examination showed no branch of the liquidus between the branches AB and BC. A very similar change of structure results on annealing a Cu-Al alloy containing 92 percent Cu.

The 55 percent Cu alloy shows a few scattered  $\alpha$ -crystals.

Fig. 13 shows the 52.2 percent alloy which is pure  $\beta$  and does not break down to a mixture of crystals even at  $300^\circ$ , though annealed for two days at that temperature.

The 50 percent alloy when quenched from  $800^\circ$  or cast in water is exactly like the 52-57 percent alloys. If chilled but moderately the white  $\gamma$ -crystals tend to be exuded from the  $\beta$  solid solution and etching develops a structure like Fig. 14. Annealing develops these  $\gamma$ -crystals as seen in Fig. 15.

In a similar way the 46.6 percent Cu alloy which is homogeneous when cast in water, shows an incipient breaking down when cast in an iron mold, Fig. 16. When annealed at  $400^\circ$  for some time it shows large masses of the white  $\gamma$ -crystals, Fig. 17.

Even casting direct into water will not make the 45 percent Cu alloy homogeneous, Fig. 18. We have now reached the composition where  $\beta$ - and  $\gamma$ -crystals appear, i. e., the lower concentration of the  $\gamma$  solid solution. Annealing at  $400^\circ$  causes the  $\beta$ -crystals to diminish greatly, Fig. 19. At 43 percent Cu casting in water shows a more plentiful amount of  $\gamma$  than at 45 percent, Fig. 20. At 41 percent traces of  $\beta$  occur, but the ingots are homogeneous  $\gamma$  from 40–31 percent Cu.

At 31 percent Cu the cast ingot shows a peculiar cracking along certain sharp lines, Fig. 21. A similar appearance is found in chill cast bronzes between 63 and 68 percent Cu, but no explanation based on experiments is now available. The 31 percent annealed alloy shows a faint trace of eutectic, Fig. 22.

From Diagram 2, it can be seen that the 28 percent alloy will show very different structures depending on its heat treatment. If quenched from above  $690^\circ$  the  $\gamma$ -crystals would be the only ones present in the ingot. Since the  $\gamma$ -crystals change into the  $\delta$  at  $690^\circ$ , the ingot quenched from below that temperature would show homogeneous  $\delta$ , while if the ingot be annealed below  $450^\circ$  it will have broken down to a mixture of  $\gamma$  and  $\delta$ . As shown in Fig. 23, the ingot annealed and quenched from  $640^\circ$  is homogeneous, being entirely made up of  $\delta$ -crystals.

Owing to the high temperature needed for this annealing, considerable zinc is lost by volatilization, and it is necessary to examine a section from the center of the ingot. In Fig. 24 is shown the 28 percent alloy, but as the section is near the surface of the ingot, one finds  $\gamma$ - and  $\delta$ -crystals. The large white masses are  $\gamma$ -crystals.

Another thing which must be avoided is the surface film formed during the polishing.<sup>1</sup> It can be removed by fairly vigorous etching, and Fig. 25 shows the 26 percent alloy after this film has been removed. The corrosion has been vigorous, and the film is entirely removed, and below it we find the outlines of the large crystals which constitute the ingot. The surface of the crystals is badly pitted, but the dark spaces will

<sup>1</sup> Beilby. Proc. Roy. Soc. London, 72, 218, 226 (1904).

become light if the crystal is rotated, so that the light strikes it differently. This last point is better shown by oblique illumination, Fig. 26. The surface of this ingot is really uniformly bright, the homogeneous coloring being entirely dependent on the angle at which the light falls upon it.

Alloys of compositions between 28 and 30 percent copper will, like the 28 percent alloys, show an entirely different structure if annealed below  $450^{\circ}$ . Thus in Fig. 27 there appears a mixture of a hard brittle and white alloy with a zinc colored one, i. e., a mixture of  $\gamma$ - and  $\delta$ -crystals. Higher magnification and careful etching do not bring out the peculiar structure of the  $\delta$ -crystals.

At 23 percent the cast alloy shows a dark ground-mass through which run fine fibers of a brilliant white constituent, Figs. 28 and 29. When annealed at  $400^{\circ}$  the structure develops into that shown in Fig. 30. This is seen to be a mixture of  $\gamma$ - and  $\delta$ -crystals. When annealed at  $640^{\circ}$  and quenched there is produced a coarse structure, Fig. 31, which consists of large rounded lobes of  $\delta$ , embedded in a dark matrix which yields no definite structure and which is liquid at the temperature of annealing. Upon quenching the cooling was, in this case, too slow to fix the  $\delta$ -crystals as homogeneous structures and they have already begun to break down. With smaller ingots which permit more rapid cooling, a homogeneous structure can be obtained, but Fig. 31 seems to be the more interesting.

The 20 percent Cu ingot cast shows an indefinite, partly broken down, mixture of crystals, which are probably mixed  $\gamma$  and  $\epsilon$  with an uncertain amount of  $\delta$ , Fig. 32. Annealed at  $400^{\circ}$  the same ingot shows a mass of  $\epsilon$  with a few scattered patches of  $\gamma$ -crystals, Fig. 33.

From 20-16 percent Cu, the appearance of the cast alloys remains much the same, Figs. 34 and 36. Upon annealing this, indefiniteness gives place to a homogeneous structure (Figs. 35, 37 and 39) which is the  $\epsilon$  solid solution.

At 14 percent the amount of  $\delta$  formed in the freezing alloy, before the quadruple point is reached, is so small that it has had

time to change over and we begin to see the  $\epsilon$ -crystals as original constituents of the alloy on solidifying, Fig. 38. These alloys crack upon annealing, which is due to the absorption of the inter-crystalline mass by the crystals. As no inter-crystalline masses occur at 14 percent, we are inclined to extend the lower limit of  $\epsilon$  somewhat below 14 percent, Fig. 39.

Between 12-2.5 percent Cu the cast and annealed samples are much alike. This is due to the fact that the phase which separates first is stable at all temperatures below the freezing-point, Figs. 40-45.

The alloys from 2.5 percent Cu to pure zinc are all similar in structure. They are homogeneous when annealed. Occasionally there will be seen a peculiar kind of crystal, Fig. 46. These have been observed in some rods of C. P. zinc purchased from Bender and Hobein for E. M. F. determinations, so that they are evidently not due to the copper. Their real nature is unknown, but may be related to the allotropic forms of zinc, a subject which has been entirely neglected.

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A few general remarks as to the methods employed in this investigation may not be out of place.

After polishing the sections, care must be taken that the surface film formed is removed before drawing conclusions as to the nature of the crystals. In some cases, as in the 20-40 percent Cu alloys, this film is quite persistent, and in striving to remove a patch of it the previously freed surfaces may be badly corroded. Nevertheless repeated polishings and etchings will make clear the nature of the alloy, though it may not lend itself readily to photographic presentation.

The etching fluid used was usually a mixture of ammonium hydroxide and hydrogen peroxide, diluted according to the requirements of the alloy. This dilution is best determined by experience. In a few cases diluted potassium hydroxide was used. Potassium cyanide was found very satisfactory for removing oxide in order to allow color determinations.

The annealings were done in an electric furnace, either that

of Heraeus or one made by winding nickel wire about an ordinary porous cell, such as is used for electrolytic work. The size of the nickel wire was No. 23 (B. and S. gauge) and the successive windings were separated by asbestos paper. Four coils of wire were used and this furnace, when well packed, will attain a temperature of  $800^{\circ}\text{C}$  on less than three amperes at 110 volts. It will not last long at that temperature, but at the lower temperatures of  $500^{\circ}$  to  $700^{\circ}$  will usually last several weeks. Several have stood  $800^{\circ}$  for two or three days, but ordinarily twenty-four hours at  $800^{\circ}$  is the limit, the nickel wire becoming brittle and breaking on cooling down. The furnace is cheap, easily repaired and much more economical than the larger Heraeus furnaces. It is always necessary to check the composition of the alloys by analysis and this has been done in all cases.

### III. The Color of Copper-Zinc Alloys

In the table of properties collated by the Alloys Committee of the United States Board,<sup>1</sup> certain brasses show abnormal colors. It will be noticed that in all cases these abnormal colors were observed in brasses whose chemical composition had not been checked analytically. The colors observed by the U. S. Board are the correct ones.

The following table (I), taken from the above report, gives the true colors for these alloys. Any copper-zinc alloys whose colors as related to composition do not agree with this table, do not have the composition which is attributed to them and should be investigated analytically.

In this table we have omitted all data where the composition of the test piece was not determined analytically.

There is but little difference in color between the annealed and cast samples, so that a more general classification, based on color alone, is shown in Table II, the phase present in excess being given first.

From 61-43 percent Cu, rapidly chilled brasses are of a uniform reddish color. This color is due to the  $\beta$ -crystals and is a deeper red than the alloy containing 90 percent copper.

<sup>1</sup> U. S. Board. Report of the Alloys Committee. See *Thurston's Alloys, Brasses and Bronzes*, p. 166.

TABLE I.

Composition by analysis		Density	Color	Fracture	Tensile strength pounds per sq. in.	Relative ductility (Thurston)
Cu	Zn					
100.0	—	8.874	red	fibrous	27800	30.8
97.8	1.8	8.791	yellow red	vesicular	27240	118.9
92.3	7.6	8.746	" "	"	—	—
90.5	9.4	8.773	" "	"	—	169.1
73.2	26.4	8.465	yellow	earthy	31580	88.7
71.2	28.5	8.444	"	"	30510	77.8
69.7	30.0	8.384	"	"	28120	48.1
66.2	33.5	8.371	red yellow	"	37800	72.8
63.4	36.3	8.411	" "	"	48300	60.6
60.9	38.6	8.405	" "	"	41065	49.0
58.5	41.1	8.363	" "	"	50450	12.1
55.1	44.1	8.283	" "	"	44280	19.5
54.8	44.7	8.301	" "	coarsely granular	46400	7.4
49.6	50.1	8.291	" "	" "	30990	3.1
48.9	50.8	8.216	pinkish gray	" "	26050	0.36
47.5	52.2	—	" "	" "	24150	0.26
43.3	56.2	8.035	" "	finely granular	9710	0.02
41.3	58.1	8.061	silvery white	vitreous conchoidal	3727	0.01
38.3	61.0	7.982	" "	" "	3087	0.02
36.6	62.7	7.974	" "	" "	2656	0.006
35.6	63.7	7.966	" "	" "	2397	0.11
32.9	66.2	7.811	" "	" "	1774	0.005
29.2	70.8	7.766	light gray	vitreous	6414	0.009
22.1	77.4	7.416	bluish gray	finely granular	7000	0.004
20.8	77.6	7.418	" "	" "	9000	0.002
17.4	81.6	7.225	" "	" "	5350	0.003
14.1	85.7	7.163	" "	" "	8500	0.004
12.1	86.6	7.238	" "	" "	12413	0.009
10.3	88.8	7.253	" "	" "	14450	0.1
7.2	92.0	7.131	" "	" "	10650	8.04
4.3	94.5	7.108	" "	" "	18065	0.84

In determining the color one must avoid oxidized surfaces, which are quite misleading. Etching with ammonia, or acids, causes a marked change in color, and such surfaces cannot be used in color determinations. The freshly filed surface gives the truest color. However a difference will be noticed between the filed and fractured surface of alloys containing 43 and 60



percent copper, and especially annealed alloys between 43 and 50 percent Cu. This color difference is due to the fact that the fracture occurs along the crystal faces. These faces being covered with the white  $\gamma$ -crystals, appear lighter than the corresponding filed surface. From 54–60 percent Cu a similar color difference is observed, but here the red crystals are coated with the yellow  $\alpha$ -crystals. This difference between the filed and fractured surface can be much more readily seen in the case of bronzes. A bronze containing 76 percent copper shows a gray fracture and a bright yellowish red filed surface. The cause is the same in both cases.

TABLE II.

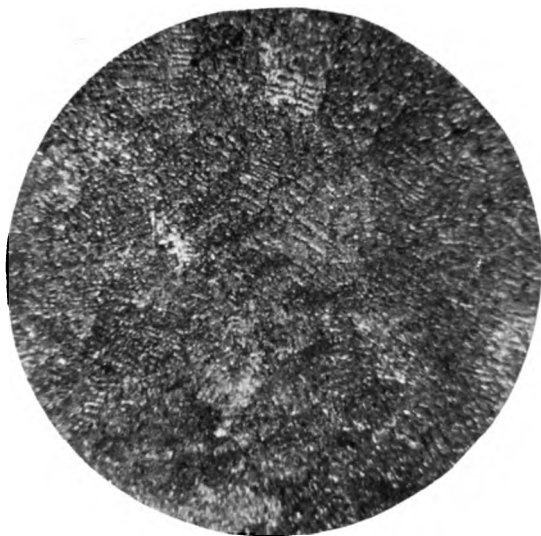
Composition % Cu	Crystals present cast brass	Color	Color of fracture
100–63	$\alpha + \beta$	red, changing to full yellow	yellow
63–54	$\beta + \alpha$	reddish yellow with a yellowish cast	yellowish red
54–51	$\beta$	reddish yellow	yellowish red
51–43	$\beta + \gamma$	reddish yellow	yellowish red
42–40	$\gamma + \beta$	yellowish red	silvery with pinkish tinge
40–30	$\gamma$	silvery	silvery, very brilliant
30–20	$\gamma + \epsilon + \delta$	silvery gray to bluish gray	silvery gray, be- coming duller
20–13	$\epsilon$	bluish gray	bluish gray
13–2.5	$\epsilon + \eta$	bluish gray, be- coming lighter	zinc
2.5–0	$\eta$	zinc	zinc

Owing to the rapid volatilization of zinc the skin of all castings is richer in copper than is the interior. Consequently this outer skin should be removed in order to observe the true color. This difference is very marked with alloys of between 35 and 40 percent copper content.

#### Summary

In this research the following results have been obtained : —

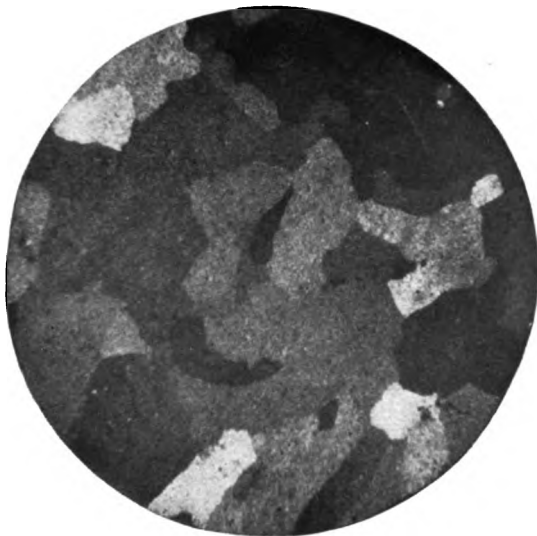
1.



83.3 % Cu. C.

× 40

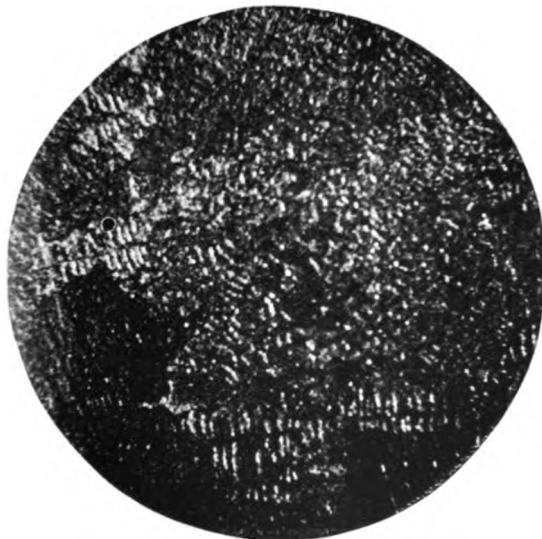
2.



79.5 % Cu. A.

× 40

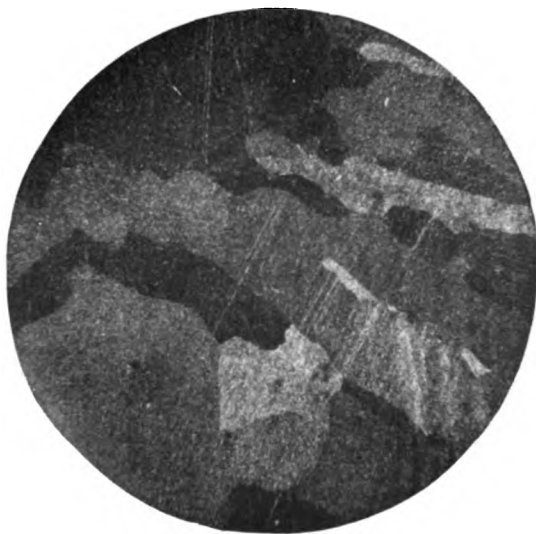
3.



66.3 % Cu. C.

× 40

4.

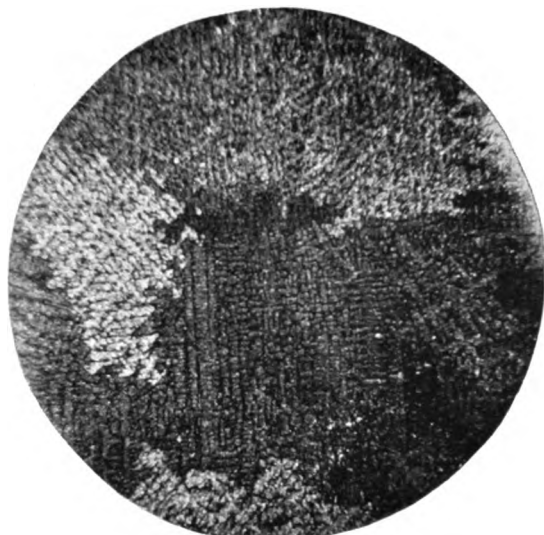


66.3 % Cu. A.

× 40



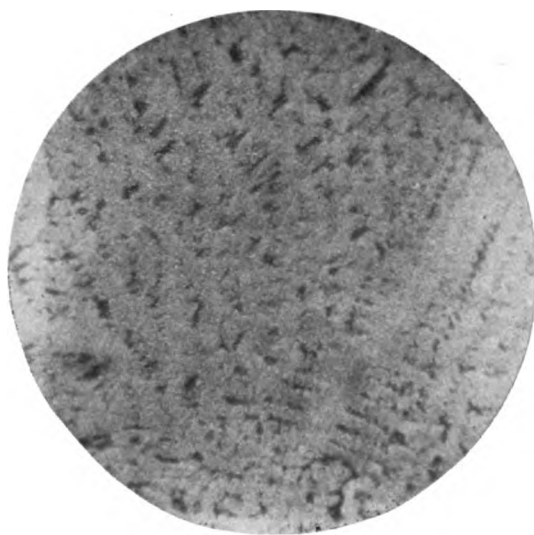
5.



63.8 % Cu. C.

× 40

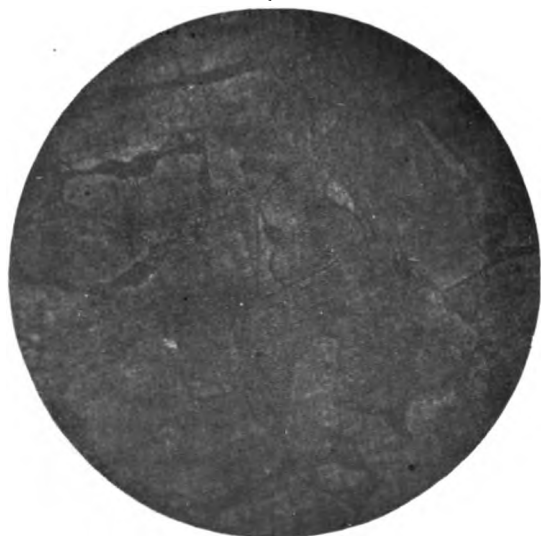
6.



63.8 % Cu. C.

× 180

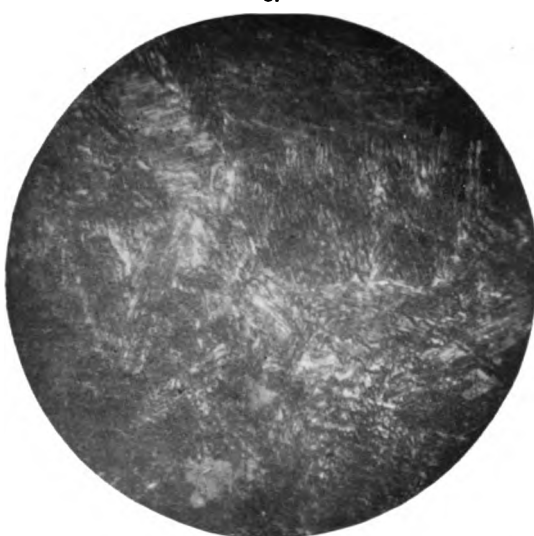
7.



63.8 % Cu. Aq. 800°

× 180

8.

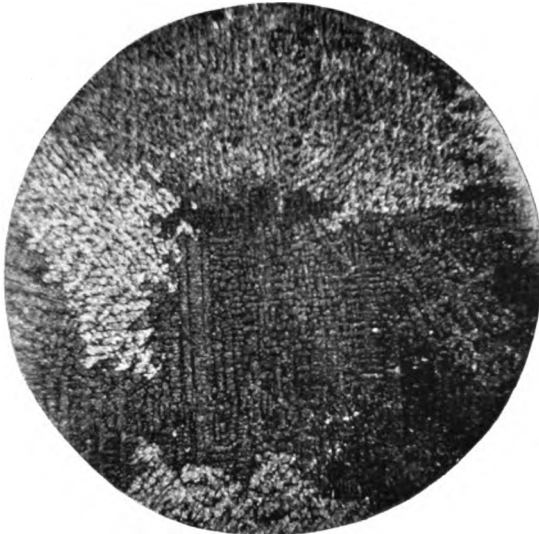


62 % Cu. W. C.

× 180



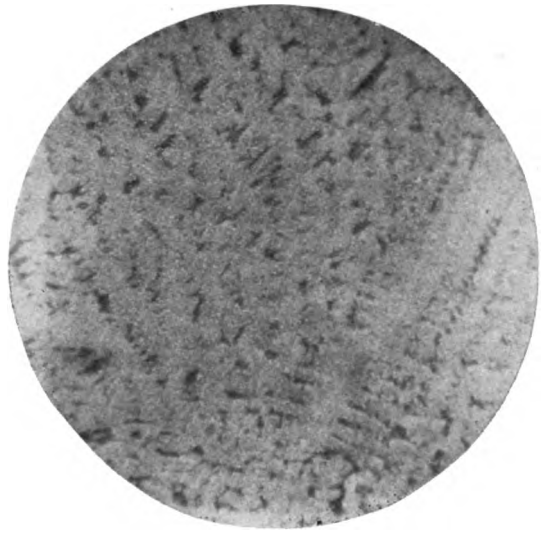
5.



63.8 % Cu. C.

× 40

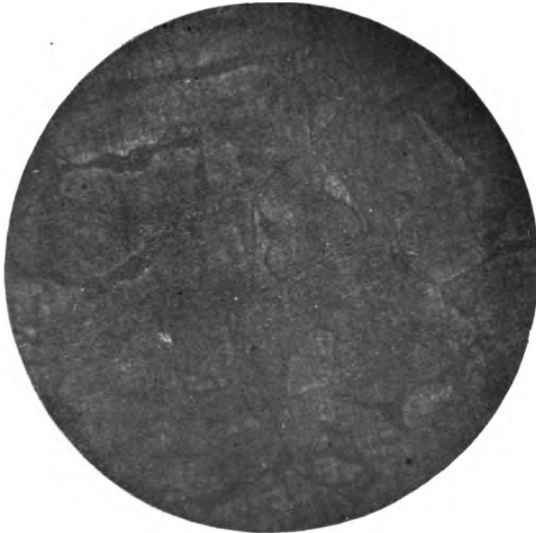
6.



63.8 % Cu. C.

× 180

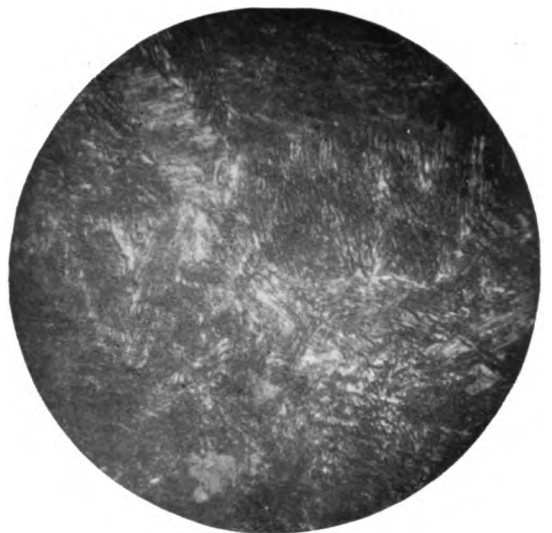
7.



63.8 % Cu. Aq. 800°

× 180

8.

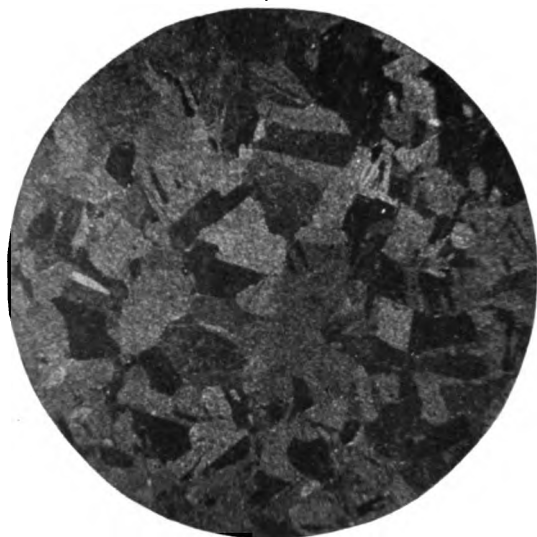


62 % Cu. W. C.

× 180



9.



62.7 % Cu. A.

× 180

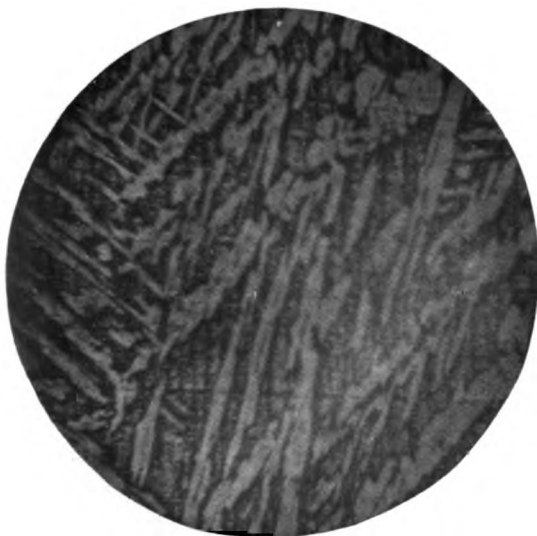
10.



58.5 % Cu. Aq. 800°.

× 80

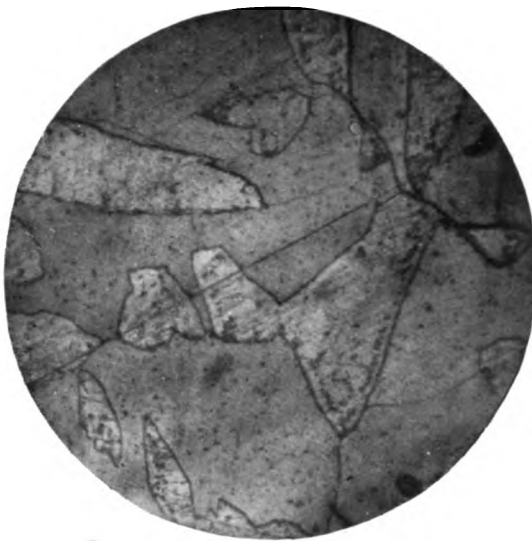
11.



58.5 % Cu. S.C.

× 180

12.



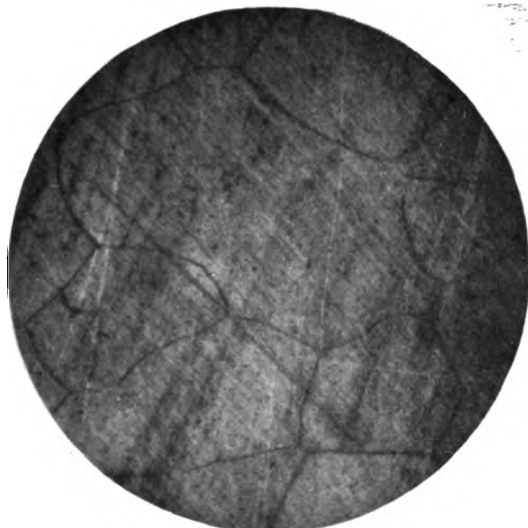
56.9 % Cu. A.

× 180





13.



52.2 % Cu. A.

× 80

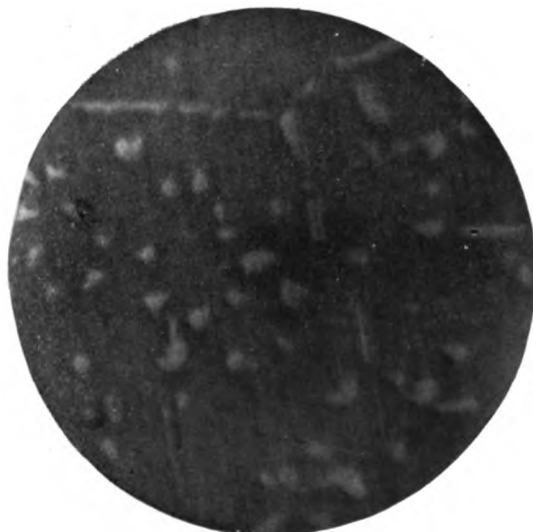
14.



50 % Cu. C.

× 180

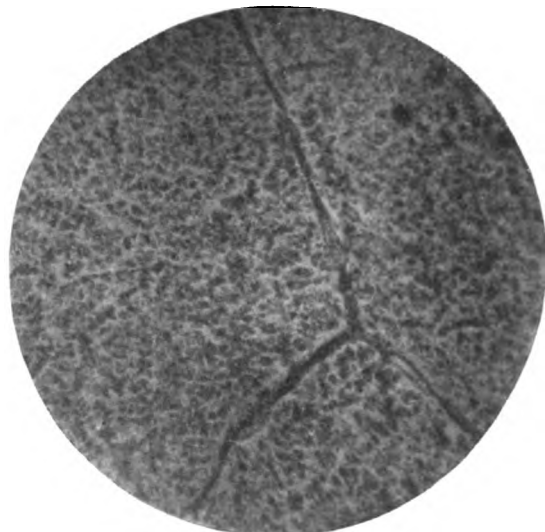
15.



50 % Cu. A.

× 180

16.

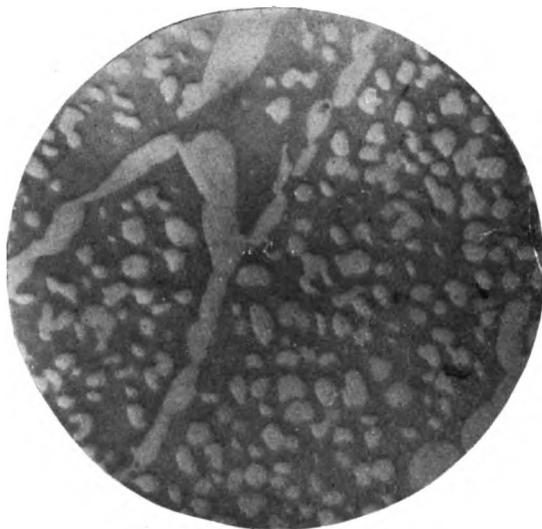


46.6 % Cu. C.

× 180



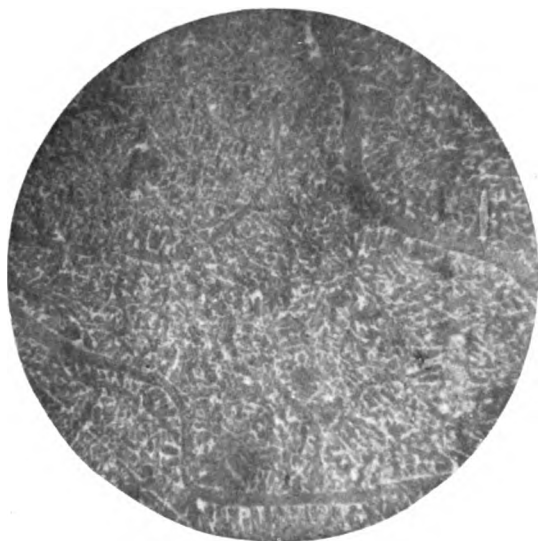
17.



46.6 % Cu. A.

× 180

18.



45 % Cu. C

× 180

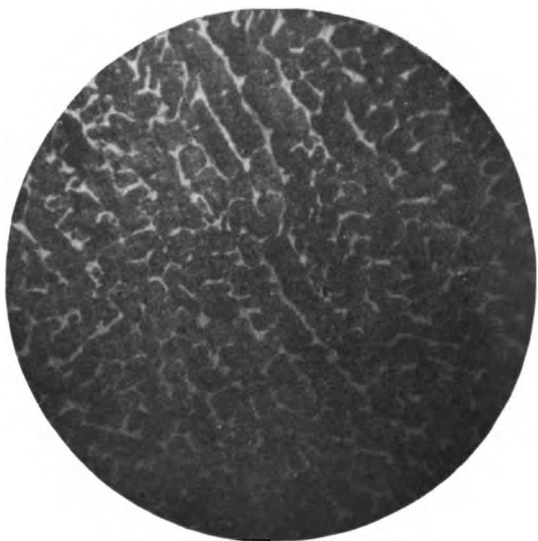
19.



43.9 % Cu. A.

× 80

20.

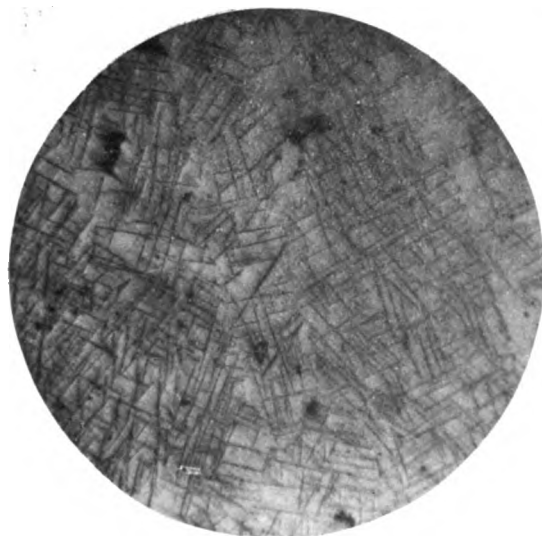


43 % Cu. W. C

× 180



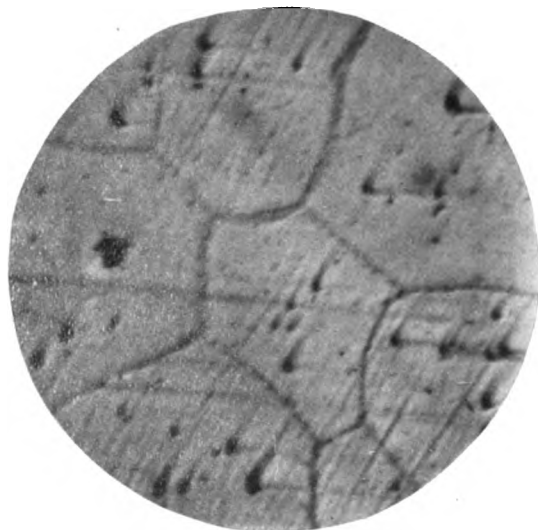
21.



31 % Cu. C.

× 100

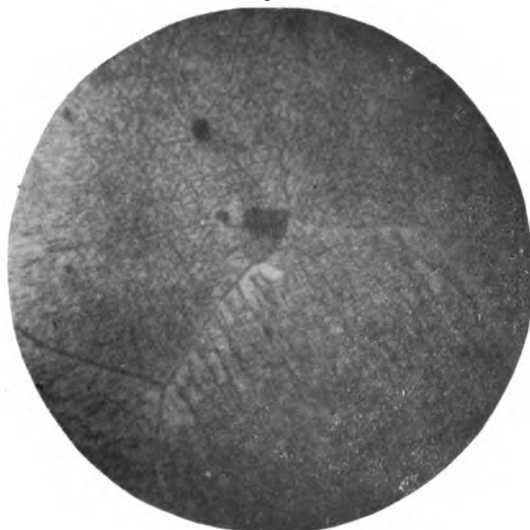
22.



31 % Cu. A.

× 80

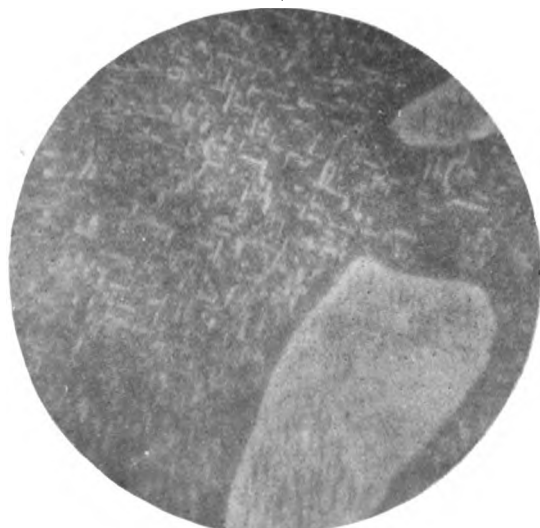
23.



28 % Cu. Aq. 640°.

× 180

24.

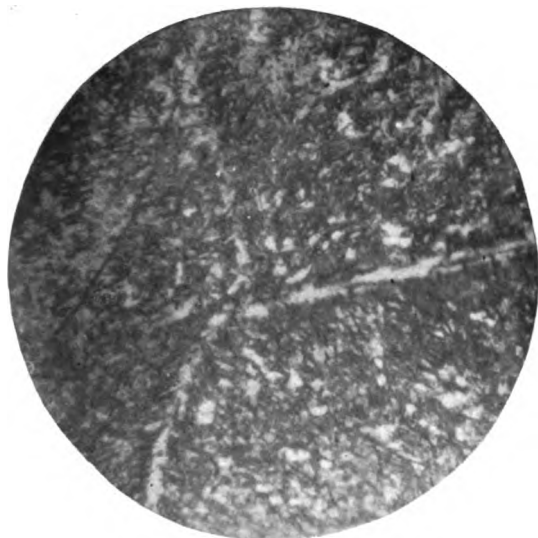


28 % Cu. Aq. 640°.

× 180



25.



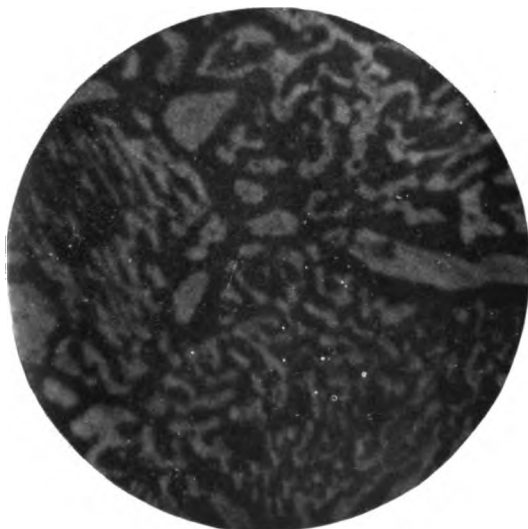
26 % Cu. Aq. 640°. × 180

26.



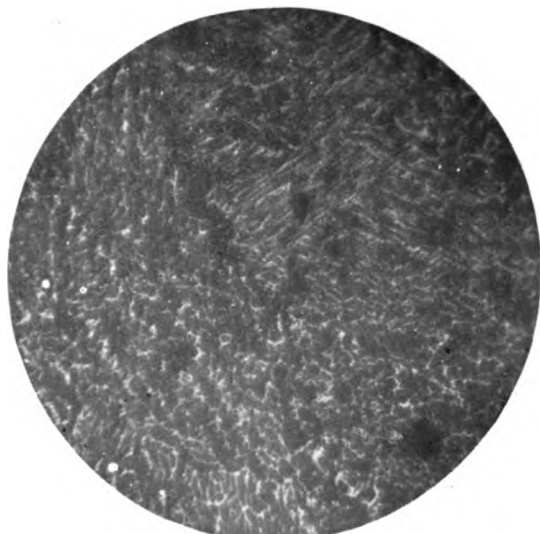
26 % Cu. Aq. 640°. × 80

27.



26 % Cu. A. × 80

28.

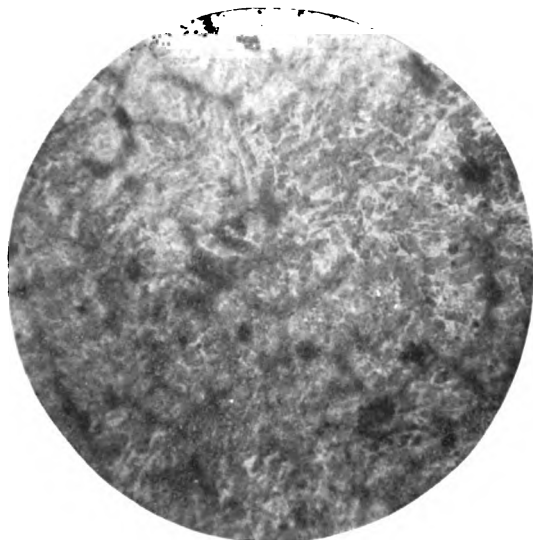


23.1 % Cu. C × 180





29.



22.9 % Cu. C.

× 180

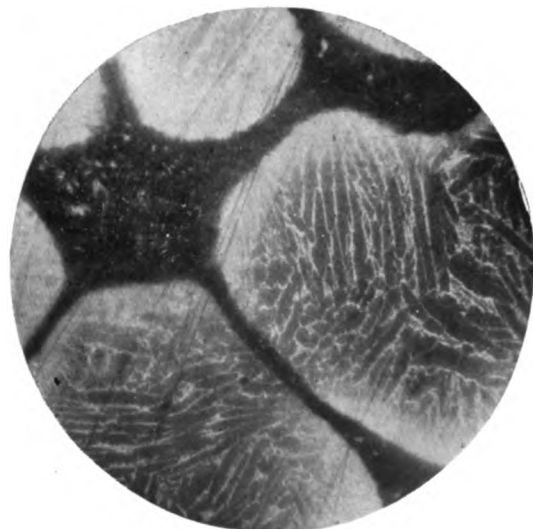
30.



23.1 % Cu. A.

× 180

31.



23 % Cu. Aq. 640°.

× 180

32.

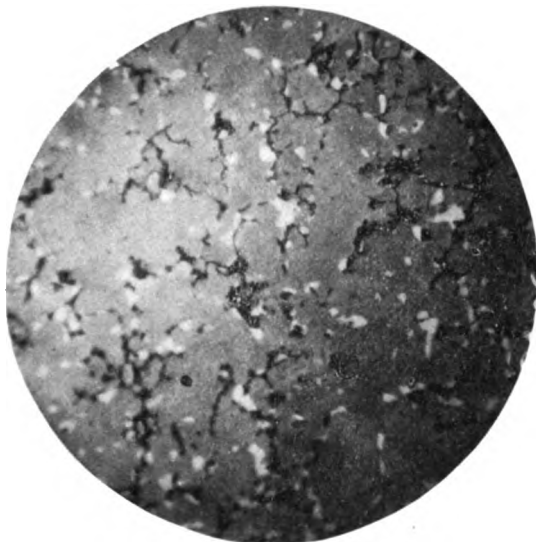


20 % Cu. C.

× 180



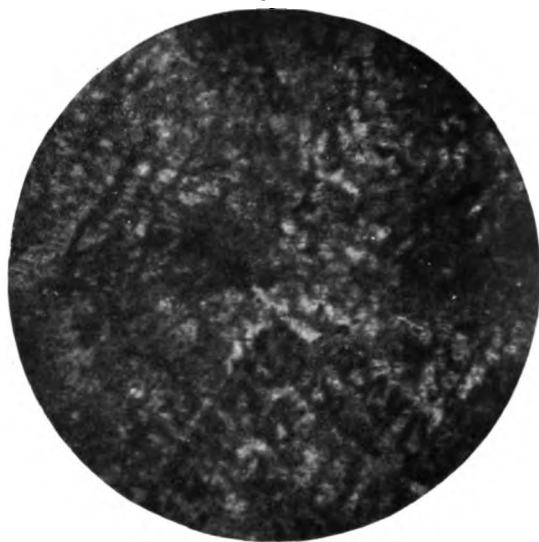
33.



20 % Cu. A.

× 180

34.



16 % Cu. C.

× 180

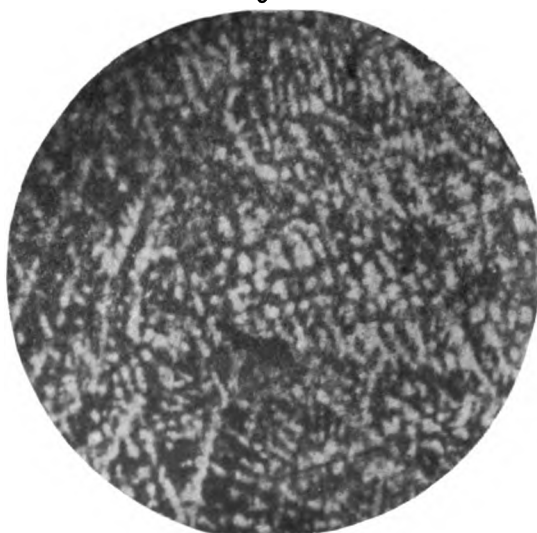
35.



18 % Cu. A.

× 80

36.

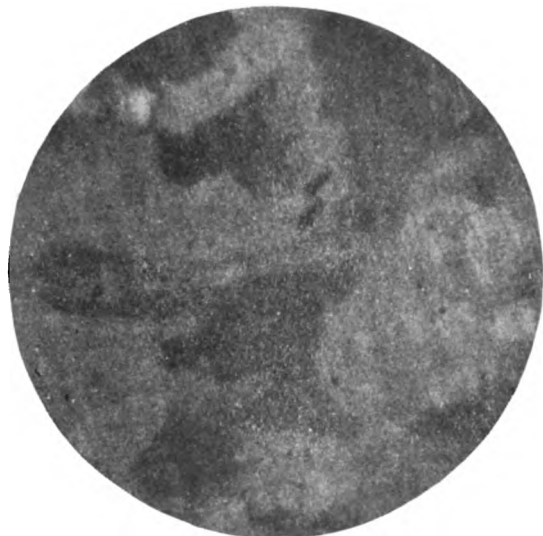


16 % Cu. C.

× 180



37.



16 % Cu. A.

× 80

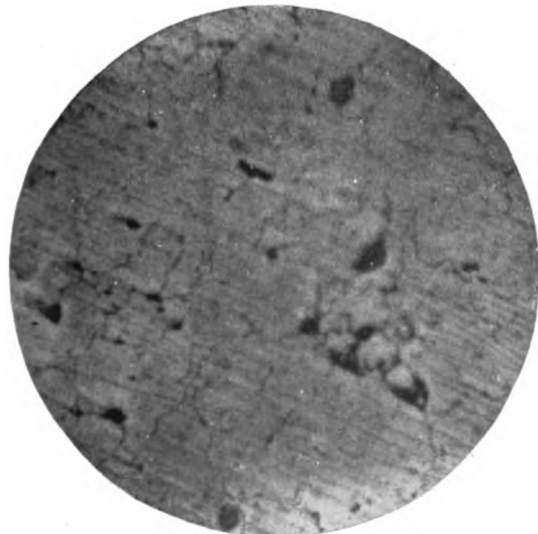
38.



14 % Cu. C.

× 180

39.



14 % Cu. A.

× 440

40.

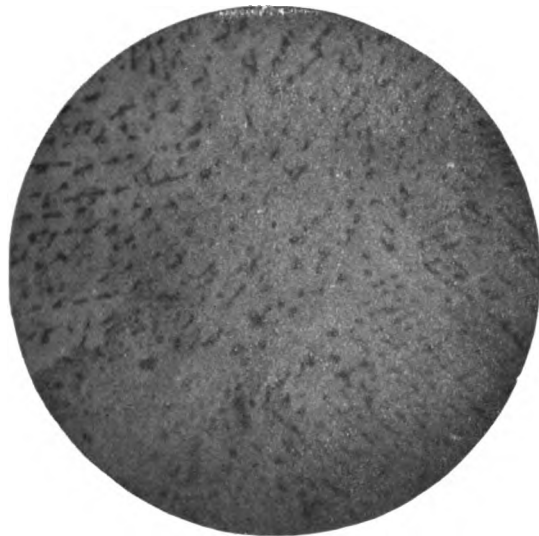


12 % Cu. C.

× 180



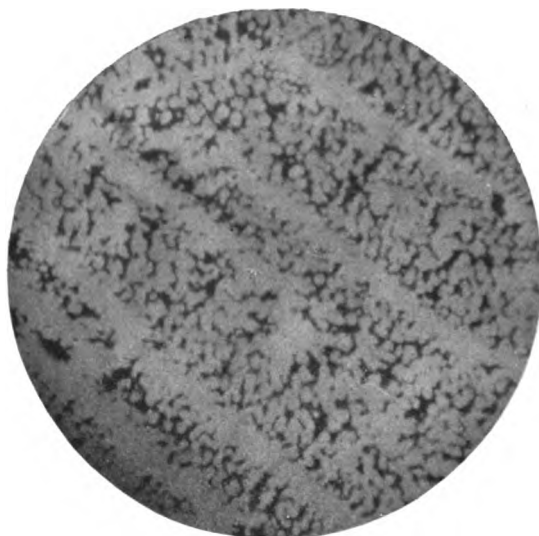
41.



12 % Cu. A.

× 180

42.



10 % Cu. C.

× 180.

43.



10 % Cu. A.

× 180

44.



8.8 % Cu. C.

× 180





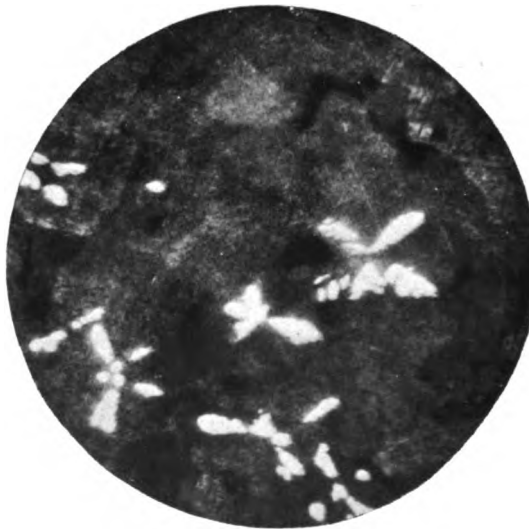
45.



5 % Cu. C.

× 180

46.



2 % Cu. C.

× 450



1. Copper and zinc unite to form six series of solid solutions, which have been distinguished as  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\epsilon$ , and  $\eta$ . The limiting concentrations of these solid solutions have been determined.
2. The equilibrium diagram for the system has been presented.
3. There are no "definite compounds" between copper and zinc.
4. One quadruple point overlooked by Roberts-Austen has been found.
5. The red color of brasses low in copper has been given its first accurate explanation.
6. Photomicrographs of the complete series are given, showing the effect of heat treatment on the brass.

This work was done under the direction of Prof. Bancroft, to whom the author wishes to express his gratitude for very patient criticism and advice.

The expenses incurred in the research were covered by a grant from the Carnegie Institution, to which we wish to express our appreciation.

The relation between the mechanical properties and the equilibrium relations, heat treatment, etc., will form the substance of our next report.

*Cornell University,  
May 14, 1904.*

## ON THE STABILITY OF THE EQUILIBRIUM OF BIVARIANT SYSTEMS

BY PAUL SAUREL

The following properties of an  $n$ -component univariant system are well known :

At a given temperature and under the corresponding equilibrium pressure  $n + 1$  phases can coexist in equilibrium. At the given temperature and under the corresponding pressure, the univariant system of  $n + 1$  phases admits of a continuous series of states of equilibrium in which the entropy and the volume of the system change while the total thermodynamic potential of the system and the concentrations of the phases remain unaltered. The state of equilibrium is completely determined if, in addition to the masses of the independent components, the volume or the entropy of the system be given.

By removing one of the  $n + 1$  phases of the univariant system we can form  $n + 1$  different bivariant systems. Each of these systems can be in equilibrium at a series of temperatures and under a series of pressures. The temperature and the pressure can be chosen independently, but then the state of equilibrium of the bivariant system is completely determined.

If, starting at the temperature and under the pressure of the univariant system, we keep the pressure of any one of the derived bivariant systems constant, but vary its temperature, it will be found that the equilibrium of the bivariant system will be stable at temperatures higher than that of the original univariant system and unstable at temperatures lower than that of the univariant system, or else that the equilibrium will be unstable at the higher and stable at the lower temperatures.

In like manner, if we keep the temperature constantly equal to that of the original univariant system and allow the pressure to vary, it will be found that the equilibrium of any one of the derived bivariant systems will be stable for pressures on one side

of the pressure of the univariant system and unstable for pressures on the other side of that pressure.

The object of the present note is to establish the following two theorems, which enable us to distinguish the stable from the unstable states of equilibrium of the bivariant systems.

I. Consider the univariant system in equilibrium at a given temperature and under the corresponding pressure. Without changing the temperature or the pressure of the system let us subject it to a reversible change which increases its entropy. During this change, the masses of certain of the phases increase while the masses of the others decrease. If the mass of the  $i$ -th phase increases, then the  $i$ -th bivariant system, that is to say, the bivariant system in which the  $i$ -th phase is lacking, cannot exist in stable equilibrium under the given pressure at temperatures higher than that of the univariant system. If, on the contrary, the mass of the  $i$ -th phase diminishes, then the  $i$ -th bivariant system cannot exist at temperatures lower than that of the univariant system.

II. Consider the univariant system in equilibrium at a given temperature and under the corresponding pressure. Without changing the temperature or the pressure of the system let us subject it to a reversible change which diminishes its volume. During this change the masses of certain of the phases increase while the masses of the others decrease. If the mass of the  $i$ -th phase increases, then the  $i$ -th bivariant system cannot exist in stable equilibrium at the given temperature under pressures greater than that of the univariant system. If, on the contrary, the mass of the  $i$ -th phase diminishes, then the  $i$ -th bivariant system cannot exist under pressures lower than that of the univariant system.

To establish the first theorem, consider the  $i$ -th bivariant system in equilibrium at the temperature and under the pressure of the original univariant system. Without changing the temperature or the pressure we can, by changing the entropy of the system, cause the  $i$ -th phase to appear; this will require either an increase or a decrease in the entropy. Suppose that an in-

crease of entropy causes the  $i$ -th phase to appear. Denote the thermodynamic potential, the entropy and the volume of the system in the first state of equilibrium by  $\Phi_1$ ,  $H_1$ ,  $V_1$ , and in the second state of equilibrium by  $\Phi_2$ ,  $H_2$ ,  $V_2$ . Then we have obviously the following relations:

$$\begin{aligned}\Phi_1 &= \Phi_2, \\ H_1 &< H_2, \\ V_1 &> V_2.\end{aligned}\tag{1}$$

If we take the system in the first state of equilibrium and if, without changing the pressure  $\Pi$ , we change the temperature  $T$ , the change in the thermodynamic potential will be given by the equation

$$d\Phi_1 = -H_1 dT.\tag{2}$$

In like manner, if we take the system in the second state of equilibrium and if, without changing the pressure, we change the temperature, the change in the potential will be given by the equation

$$d\Phi_2 = -H_2 dT.\tag{3}$$

If we suppose that the change in temperature  $dT$  is positive, conditions 1, 2, 3 yield immediately

$$\Phi_1 + d\Phi_1 > \Phi_2 + d\Phi_2.\tag{4}$$

If we remember that at a given temperature and under a given pressure a system cannot be in stable equilibrium unless its thermodynamic potential has the least value possible at that temperature and under that pressure, it follows from inequality 4 that, under a pressure equal to that of the original univariant system and at a temperature slightly higher than that of the univariant system, the  $i$ -th bivariant system cannot be in stable equilibrium. This establishes the first part of Theorem I.

Suppose that at the temperature and under the pressure of the univariant system a decrease in the entropy of the system is necessary if the  $i$ -th phase is to appear. Conditions 1 must be replaced by the following:

$$\begin{aligned}
 \Phi_1 &= \Phi_2, \\
 H_1 &> H_2, \\
 V_1 &\begin{cases} > \\ < \end{cases} V_2.
 \end{aligned}
 \tag{5}$$

If we suppose that  $dT$  is negative, conditions 5, 2, 3 yield immediately inequality 4. It follows that, under a pressure equal to that of the univariant system and at a temperature slightly lower than that of the univariant system, the  $i$ -th bivariant system cannot be in stable equilibrium. This establishes the second part of Theorem I.

Theorem II can be established by a course of reasoning in all respects similar to that just given. Instead of equations 2, 3, we now use the equations:

$$\begin{aligned}
 d\Phi_1 &= V_1 d\Pi, \\
 d\Phi_2 &= V_2 d\Pi;
 \end{aligned}$$

and instead of the conditions 1 and 5 we now have to consider the conditions

$$\begin{array}{ccc}
 \Phi_1 = \Phi_2, & & \Phi_1 = \Phi_2, \\
 H_1 \begin{cases} > \\ < \end{cases} H_2, & \text{and} & H_1 \begin{cases} > \\ < \end{cases} H_2, \\
 V_1 > V_2, & & V_1 < V_2.
 \end{array}$$

With the first set of conditions we take  $d\Pi$  positive, with the second set negative. In each case we obtain inequality 4.

The theorems which we have just established may be considered as consequences of the well-known theorems of Moutier<sup>1</sup> and of Robin.<sup>2</sup> They can, however, be traced further back, for Gibbs in his memoir "On the Equilibrium of Heterogeneous Substances," has given a complete discussion<sup>3</sup> of the application of these theorems to binary and ternary bivariant systems.

*New York, April 18, 1904.*

<sup>1</sup> Moutier. Bulletin de la Société philomathique, (3) 1, pp. 39 and 96 (1877). Duhem. Mécanique chimique, 1, 191. Mécanique chimique, 1, 158.

<sup>2</sup> Robin. Bulletin de la Société philomathique, (7) 4, 24 (1882). Duhem.

<sup>3</sup> Trans. Conn. Acad. 3, pp. 178-183 (1876).



## REVIEWS

*The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry.*

### General

**High vacua for chemical distillation.** *E. Erdmann. Ber. chem. Ges. Berlin, 36, 3456 (1903).* — The author fills his distilling apparatus with pure carbon dioxide from solid carbon dioxide and then condenses it with liquid air. In this way he gets a very high vacuum with little trouble and expense.

*W. D. B.*

**On obtaining a vacuum without powerful pumps or liquid air.** *F. Krafft. Ber. chem. Ges. Berlin, 37, 95 (1904).* — An apparatus is described in which the air is first displaced by carbon dioxide. The pressure is then lowered to 20 mm by means of a water pump, the carbon dioxide removed with caustic potash solution and the water vapor by a freezing mixture of carbon dioxide and ether. In this way it is easily possible to get a vacuum showing the green cathode light.

*W. D. B.*

### One-Component Systems

**Fluid crystals.** *R. Schenck and E. Eichwald. Ber. chem. Ges. Berlin, 36, 3873 (1903).* — It has been maintained by Rotarski and by Tammann that the fluid crystals of *p*-azoxyanisole are really due to the presence of an impurity of azoanisole. The authors have repeated the work, taking great care to obtain pure material. Their results show that the fluid crystals are not due to impurities.

*W. D. B.*

**The vaporizing and boiling of metals in the vacuum of the cathode light.** *F. Krafft. Ber. chem. Ges. Berlin, 36, 1690 (1903).* — By using quartz vessels and an electric furnace the author has not only vaporized but actually distilled a number of metals under the vacuum of the green cathode light. Since the boiling-points change markedly with the height of the vapor column, no absolute boiling-points are given. There seems also to have been marked superheating. The substances distilled were zinc, cadmium, selenium, tellurium, lead, antimony and bismuth, while silver, copper and gold were vaporized.

*W. D. B.*

**The boiling of sulphur, selenium and tellurium in the vacuum of the cathode light.** *F. Krafft and L. Merz. Ber. chem. Ges. Berlin, 36, 4344 (1903).* — Under the vacuum of the green cathode light, the authors obtain the following boiling-points: sulphur, 140°; selenium, 310°; tellurium, 478°. Different boiling-points are observed under 40 mm vapor column for 'normal' and for viscous sulphur. No reference is made to Malus.

*W. D. B.*

The vapor pressure of fluosilicic acid. *E. Baur and A. Glaessner. Ber. chem. Ges. Berlin, 36, 4215 (1903).* — At  $100^{\circ}$  fluosilicic acid,  $\text{H}_2\text{SiF}_6$ , is about two-thirds dissociated. *W. D. B.*

On J. Thomsen's supposed preparation of carbon monosulphide. *A. Stock and H. Küchler. Ber. chem. Ges. Berlin, 36, 4336 (1903).* — It is shown that what Thomsen believed was carbon monosulphide (7, 483) was really a mixture of nitrogen and carbon bisulphide, probably containing some carbon dioxide. *W. D. B.*

#### Two-Component Systems

Regularities in the composition of the lowest melting mixtures of inorganic salt pairs. *O. Ruff and W. Plato. Ber. chem. Ges. Berlin, 36, 2357 (1903).* — The authors have made approximate determinations of the freezing-point curves for a number of pairs of inorganic salts. Unfortunately they give only the first break in the cooling curve. The regularities observed in the composition of the eutectics are about what one would expect from the melting-points of the salts. In fact, the data appear much more valuable than the conclusions. *W. D. B.*

The chlorides of sulphur. *O. Ruff and G. Fischer. Ber. chem. Ges. Berlin, 36, 418 (1903).* — The freezing-point curve for sulphur and chlorine has been determined. There are two maxima, corresponding to the melting-points of sulphur monochloride,  $-80^{\circ}$ , and sulphur tetrachloride,  $-30.5^{\circ}$ . There must be another maximum for a mixture containing over 93 percent chlorine, but this was not determined. There is no evidence for the existence of a dichloride. *W. D. B.*

The bromides of sulphur. *O. Ruff and G. Winterfeld. Ber. chem. Ges. Berlin, 36, 2437 (1903).* — The addition of bromine to  $\text{S}_2\text{Br}_2$  lowers the freezing-point until a eutectic is reached at  $-52^{\circ}$  and a composition of about 80 percent bromine. Another branch was followed from here to 93 percent bromine. From this the authors conclude that  $\text{S}_2\text{Br}_2$  is the only compound between sulphur and bromine. It is by no means certain that there is not a quadruple point at about 93 percent bromine, in which case the authors' conclusions are faulty. *W. D. B.*

The molecular weight of solid phosphorus hydride. *R. Schenck and E. Buck. Ber. chem. Ges. Berlin, 37, 915 (1904).* — Solid phosphorus hydride,  $(\text{P}_2\text{H})_n$ , dissolves to a certain extent in yellow phosphorus. From the lowering of the freezing-point the authors calculate a molecular weight corresponding to the formula  $\text{P}_{17}\text{H}_8$ . *W. D. B.*

A new method for determining the solidification point for fused electrolytes. *O. Liebknecht and E. Nilsen. Ber. chem. Ges. Berlin, 36, 3718 (1903).* — The authors determine resistance-temperature curves instead of temperature-time curves. It is not easy to see how this can give anything except the eutectic with any degree of accuracy and any crystallization between or on the electrodes would throw everything out. *W. D. B.*

The composition and temperature of liquid air. *E. Erdmann. Ber. chem.*

*Ges. Berlin*, 37, 1192 (1904). — It is shown that the composition of liquid air from a Hampson machine may vary between 28 and 57 percent oxygen, depending on whether the liquid is drawn off every ten minutes or continuously.

W. D. B.

**Preparation and properties of liquid oxygen.** *E. Erdmann and F. Bedford. Ber. chem. Ges. Berlin*, 37, 1184 (1904). — The authors find that pure oxygen takes up nitrogen from the air. This will of course be the case whenever the vapor in contact with the liquid oxygen contains more nitrogen than corresponds to equilibrium.

W. D. B.

**The solubility of nitrogen in liquid oxygen.** *A. Stock. Ber. chem. Ges. Berlin*, 37, 1432 (1904). — It is pointed out that the results of Erdmann and Bedford (preceding review) are exactly what were to have been expected from Baly's data.

W. D. B.

**Determination of the molecular weight of metal chlorides.** *L. Rügheimer. Ber. chem. Ges. Berlin*, 36, 3030 (1903). — In boiling bismuth chloride, the chlorides of sodium, barium, strontium, manganese, cobalt and copper show molecular weights corresponding to their formulas.

W. D. B.

**Boiling-point constant for nitrobenzene.** *P. Bachmann and K. Dziewonski. Ber. chem. Ges. Berlin*, 36, 971 (1903). — The boiling-point constant for nitrobenzene is found to be 50.1° instead of 46° as found by Biltz. To get good results the boiling tube must be jacketed.

W. D. B.

**The boiling-point constant for nitrobenzene.** *H. Biltz. Ber. chem. Ges. Berlin*, 36, 1110 (1903). — It is pointed out that the author's earlier value of 46 (preceding review) for the boiling-point constant of nitrobenzene was revised in 1901 and changed to 50.4.

W. D. B.

**Modification of Landsberger's apparatus.** *A. Lehner. Ber. chem. Ges. Berlin*, 36, 1105 (1903). — In this apparatus the vapors are condensed and returned beneath the level of the boiling liquid in the outer jacket. This means great danger of breaking.

W. D. B.

**A modification of the new Beckmann boiling-point apparatus with vapor heating.** *G. Walther. Ber. chem. Ges. Berlin*, 37, 78 (1904). — This is a modified McCoy apparatus in which the condensed vapor is returned. Since the boiling-tube, the heating jacket and the cooler form three separate pieces, the apparatus is relatively easy to construct and fairly cheap. It has the disadvantage, common to the other forms, of returning the condensed vapor at the bottom of the heating jacket.

W. D. B.

**Determination of molecular weights by Landsberger's method.** *R. Meyer and P. Jaeger. Ber. chem. Ges. Berlin*, 36, 1555 (1903). — This is an old-style apparatus in which a burner is placed under the boiling-point vessel to prevent excessive condensation when acetic acid is used as a solvent.

W. D. B.

**Antimony hydride and yellow antimony.** *A. Stock and O. Guttman. Ber. chem. Ges. Berlin*, 37, 885 (1904). — Antimony hydride has a vapor-density about three percent higher than that calculated for  $\text{SbH}_3$ . When dry and not in contact with metallic antimony, it decomposes very slowly. Metallic

antimony acts as a catalytic agent and so does water vapor. Two hundred and fifty volumes of gas dissolve in 1250 volumes of water, 83 volumes of alcohol, and in one volume of carbon bisulphide. Contrary to the previous reports, the gas is very poisonous, quite as much so as arsine. When oxygen is passed into liquid antimony hydride at  $-90^{\circ}$ , small quantities of a very instable yellow modification of antimony are formed.

W. D. B.

The calculation of combustion analyses of gases. *A. Wohl. Ber. chem. Ges. Berlin, 37, 429 (1904).*— Since the volume occupied by carbon dioxide is 0.6 percent less than it should be with reference to oxygen, it follows that calculations of gas mixtures based on Avogadro's law are liable to lead to error. The author suspects an error of nearly two percent in analyses made by Dennis and Hopkins. The author has not made any experiments on the behavior of mixtures of gases. In calculating analyses one makes use both of Avogadro's law and of Dalton's law.

W. D. B.

#### Multi-Component Systems

On solubility and decomposition of double salts in water. *E. Rimbach. Ber. chem. Ges. Berlin, 37, 461 (1904).*— Solubility determinations for a large number of uranyl double salts. In every case a temperature range could be found within which the double salts were not decomposed by water.

W. D. B.

The solubility of neutral and acid alkali formates. *E. Groschuff. Ber. chem. Ges. Berlin, 36, 1783 (1903).*— Solubility determinations for the neutral and acid formates of sodium and potassium, and of neutral lithium formate in water and in formic acid at different temperatures.

W. D. B.

Solubility of acid ammonium formate. *E. Groschuff. Ber. chem. Ges. Berlin, 36, 4351 (1903).*— The author has prepared an acid ammonium formate and has determined the solubility curve for ammonium formate in water and in acetic acid from  $-10^{\circ}$  to  $+105^{\circ}$ .

W. D. B.

Solubility of acid nitrates. *E. Groschuff. Ber. chem. Ges. Berlin, 37, 1486 (1904).*— The author has determined solubility curves for potassium and ammonium nitrates in nitric acid; also for  $\text{NH}_4\text{NO}_3\cdot\text{HNO}_3$ ,  $\text{NH}_4\text{NO}_3\cdot 2\text{HNO}_3$ ,  $\text{KNO}_3\cdot\text{HNO}_3$ , and  $\text{KNO}_3\cdot 2\text{HNO}_3$  in water.

W. D. B.

The solubility in acetic acid of some salts of the alkaline earths with organic acids. *W. Herz and G. Muhs. Ber. chem. Ges. Berlin, 36, 3715 (1903).*— Solubility determinations in aqueous acetic acid of the tartrates and oxalates of calcium, strontium and barium. The measurements were all made at  $26^{\circ}$ – $27^{\circ}$ .

W. D. B.

The solubility of the hydroxides of aluminum, beryllium and iridium in ammonia and the amine bases. *C. Renz. Ber. chem. Ges. Berlin, 36, 2751 (1903).*— In methyl, ethyl, dimethyl and diethyl amine aluminum hydroxide is readily soluble. The author believes that aluminum hydroxide occurs in two modifications, only one of which is soluble in ammonia. Beryllium hydroxide is insoluble in ammonia and the amines. Iridium hydroxide dissolves in dimethyl or diethyl amine solutions to which some hydrochloric acid has been added.

W. D. B.

**The sulphates of tetravalent cerium.** *R. J. Meyer and A. Aufrecht. Ber. chem. Ges. Berlin, 37, 140 (1904).* — Concentrated sulphuric acid reacts with ignited cerium dioxide, forming anhydrous ceric sulphate. Aqueous sulphuric acid forms an acid cerous ceric sulphate, which on recrystallizing from slightly acid solutions change into cerous sulphate. *W. D. B.*

**A simple process for preparing barium nitrite.** *O. N. Witt and K. Ludwig. Ber. chem. Ges. Berlin, 36, 4384 (1903).* — The authors mix barium chloride with twice the equivalent quantity of sodium nitrite in presence of a little hot water. Sodium chloride precipitates and barium nitrite can be obtained nearly pure on cooling. The yield of pure, twice-crystallized barium nitrite is 85 per cent. *W. D. B.*

**The preparation of salts by double decomposition.** *W. Meyerhoffer. Ber. chem. Ges. Berlin, 37, 261 (1904).* — It is pointed out that the recent experiments of Witt and Ludwig (preceding review) on the preparation of barium nitrite become perfectly intelligible when considered from the point of view of the phase rule, while one does not accomplish much by starting from the electrolytic dissociation theory. *W. D. B.*

**On the preparation of barium nitrite.** *O. N. Witt and K. Ludwig. Ber. chem. Ges. Berlin, 37, 382 (1904).* — The authors dispute the statement of Meyerhoffer (preceding review) that the consideration of their experiments from the point of view of the phase rule is an advantage. *W. D. B.*

**The theory of reciprocal salt pairs.** *W. Meyerhoffer. Ber. chem. Ges. Berlin, 37, 1116 (1904).* — This is a reply to Witt and Ludwig (preceding review). *W. D. B.*

**The distillation of fluosilicic acid.** *E. Bauer. Ber. chem. Ges. Berlin, 36, 4209 (1903).* — When aqueous fluosilicic acid is distilled in presence of an excess of silica, the ratio of HF to SiF<sub>4</sub> in the vapor is less than 2 for solutions containing over 13.3 percent H<sub>2</sub>SiF<sub>6</sub>, and is more than 2 for solutions less than 13.3 percent H<sub>2</sub>SiF<sub>6</sub>. *W. D. B.*

**The addition of halide acids to olefines in acetic acid solution.** *W. Ipatiew and Ogonowsky. Ber. chem. Ges. Berlin, 36, 1988 (1903).* — The addition of hydrobromic acid to isobutylene in aqueous solution gives a tertiary bromide only. In acetic acid solution some primary isobutyl bromide is formed. *W. D. B.*

**The reaction between formaldehyde and silver nitrate in presence of strong bases.** *L. Vanino. Ber. chem. Ges. Berlin, 36, 3304 (1903).* — When silver nitrate is added to a formaldehyde solution containing much caustic soda, there is a quantitative precipitation of silver. When the alkali is equivalent to the silver nitrate, some colloidal silver is formed and the precipitation is not quantitative. When alkali and formaldehyde are both present in great excess, there is evolution of hydrogen, presumably according to the equation



**Experiments with phosphorus.** *R. Schenck. Ber. chem. Ges. Berlin, 36, 979 (1903).* — When white phosphorus is boiled with phosphorus tribromide, it

changes to a bright red phosphorus which has taken up thirty percent of phosphorus tribromide. It is practically impossible to get pure phosphorus from this mass. This red phosphorus is not poisonous; but reacts in other ways more rapidly than white phosphorus. *W. D. B.*

**Studies on phosphorus, II.** *R. Schenck. Ber. chem. Ges. Berlin, 36, 4202 (1903).* — The black substance obtained by the action of ammonia on the new form of red phosphorus (preceding review) is now recognized to be  $P_4H_2NH_3$ . Solid phosphorus hydride reacts but slowly with ammonia. The change of white phosphorus into the red is now shown to be monomolecular, the previous result having probably been due to the red phosphorus removing the catalytic agent. *W. D. B.*

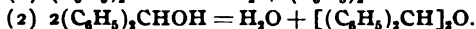
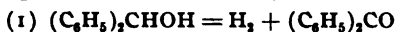
**The action of liquid ammonia on phosphorus.** *A. Stock. Ber. chem. Ges. Berlin, 36, 1120 (1903).* — When white phosphorus is treated with liquid ammonia, it changes into a fine black powder which contains nitrogen and hydrogen. On treating with acids it becomes bright orange-red. The color changes from red to black and back on successive additions of ammonia and acid. The author believes the red substance to be probably  $P_4O$ . The crystalline form is different from that of red phosphorus. It is also believed that Schenck's red material (two reviews back) is similar to the author's and that it is a compound of phosphorus. *W. D. B.*

**Pyrogenic contact reactions of organic compounds.** *W. Ipatiew. Ber. chem. Ges. Berlin, 34, 3579 (1901); 35, 1047, 1057 (1902); 36, 1990, 2003, 2014, 2016 (1903).* — In a glass tube at  $700^\circ$  and a rate of flow of 150 g per hour, ethyl alcohol does not decompose. Above  $800^\circ$  decomposition occurs with formation of some ethylene and water. The chief reaction however is the formation of hydrogen and acetaldehyde, this latter breaking down more or less completely into carbon monoxide and methane. In a platinum tube at  $780^\circ$  the ethylene formation is about one-sixth that of the aldehyde formation. With zinc at  $620^\circ$ – $650^\circ$  an 80 percent yield of aldehyde was obtained and only traces of ethylene. Ether must be heated to  $750^\circ$  with zinc before a satisfactory decomposition is obtained. The impure graphite of a graphite crucible causes alcohol to decompose at  $600^\circ$  into ethylene and water, only small amounts of aldehyde being formed. Aluminum oxide causes the decomposition of alcohol into ethylene and water at  $350^\circ$ . With amyl alcohol and aluminum oxide some trimethyl ethylene is formed. With isobutyl alcohol and aluminum oxide only one butylene is formed, while more than one is obtained when zinc chloride is used. Ethylene oxide is changed by aluminum oxide into acetaldehyde. *W. D. B.*

**The behavior of benzhydrol when heated by itself or in presence of platinum black.** *E. Knoevenagel and W. Heckel. Ber. chem. Ges. Berlin, 36, 2816 (1903).* — When benzhydrol is heated to about  $300^\circ$ , hydrogen is evolved. In presence of palladium black at  $290^\circ$  the reaction runs smoothly, benzophenone being formed. The rate of evolution of hydrogen can be expressed by the formula for a monomolecular reaction. *W. D. B.*

**The behavior of benzhydrol when heated with pulverulent copper.** *E.*

**Knoevenagel and W. Heckel.** *Ber. chem. Ges. Berlin*, 36, 2823 (1903). — Benzhydrol decomposes in two different ways :—



In presence of palladium black (preceding review) the first reaction is the only one. In presence of copper powder at 220°, the second reaction is the chief one, while both occur simultaneously at 290°, in addition to a secondary formation of tetraphenyl ethane. With increasing amounts of copper, there is a decreased benzophenone formation and an increased formation of tetraphenyl ethane. W. D. B.

**The behavior of benzoin at high temperatures and in presence of catalytic agents.** *E. Knoevenagel and A. Tomaszewski.* *Ber. chem. Ges. Berlin*, 36, 2829 (1903). — The chief solid and liquid products of the decomposition of benzoin by heat are benzil, benzophenone and benzene. With palladium black more benzene and less benzil is formed, while the reverse is the case with platinum black. Other metals have less catalytic effect than these two. Nickel, cobalt, zinc oxide and copper belong with palladium, while gold acts in a way similar to platinum. W. D. B.

**The oxidizability of platinum.** *L. Wöhler.* *Ber. chem. Ges. Berlin*, 36, 3475 (1903). — It is shown that both platinum black and very thin platinum foil oxidize readily to platinous oxide or platinous hydroxide. The oxide is soluble in hydrochloric acid. The oxidizing action of platinum black was shown to be the same as that of platinous hydroxide. W. D. B.

**Titanium oxide and its salts as reducing agents.** *E. Knecht.* *Ber. chem. Ges. Berlin*, 36, 166 (1903). — Titanium chloride,  $TiCl_3$ , is a very powerful reducing agent, more so than stannous chloride. It reduces sodium bisulphite to hydrosulphite, nitro compounds to the corresponding amines, and fumaric acid to succinic acid. W. D. B.

**A method of preparing colloidal metals.** *F. Heinrich.* *Ber. chem. Ges. Berlin*, 36, 609 (1903). — Experiments on the preparation of colloidal gold, platinum, silver and mercury, by means of pyrogallol, hydroquinone and resorcin. W. D. B.

**Application of polybasic phenols, phenol acids, aldehydes and phenol aldehydes in preparing hydrosols of gold, platinum and silver.** *L. Garbowski.* *Ber. chem. Ges. Berlin*, 36, 1215 (1903). — Gold forms colloidal solutions most readily and silver least. A carboxyl, methoxy or aldehyde group weakens the colloid-producing power of a phenol. Phloroglucine with three hydroxyl groups is more effective in producing colloidal solutions than is pyrocatechinic acid with only two hydroxyl groups. W. D. B.

**Colloidal metals of the platinum group.** *C. Paal and C. Amberger.* *Ber. chem. Ges. Berlin*, 37, 124 (1904). — Dilute caustic alkali dissolves egg albumen when heated, splitting it into two substances, one of which is precipitated by acids, while the other is not. The first is called protalbic acid and the second lysalbic acid. The alkali salts react with the salts of the heavy metals,

giving metathetical compounds which precipitate. These precipitates are soluble in alkali, the metal going into a colloidal state. From these solutions the metals can be obtained as solids which are soluble in water. These hydrosols are much more stable with regard to electrolytes than are most hydrosols. A description is given of the preparation and properties of colloidal platinum, palladium, and iridium. W. D. B.

### Velocities

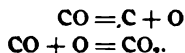
**Palladium catalysis of hydrogen peroxide.** *G. Bredig and M. Fortner. Ber. chem. Ges. Berlin, 37, 798 (1904).* — The formula for a monomolecular reaction holds for the decomposition of hydrogen peroxide by palladium. This is believed to be the result of diffusion phenomena. [On this hypothesis stirring should increase the value of the constant.] In dilute alkaline solution the reaction velocity is increased, while it is decreased by concentrated alkali. Hydrogen increases the catalytic action of palladium while carbon monoxide, iodine, hydrogen sulphide, mercuric chloride, arsine and prussic acid decrease it. In the case of carbon monoxide, there is an apparent rise above the normal after the carbon monoxide has been completely decomposed. W. D. B.

**Rate of saponification and affinity constant of diethyl malonic ester.** *H. Goldschmidt and V. Scholl. Ber. chem. Ges. Berlin, 36, 1333 (1903).* — A good reaction velocity constant was obtained for the saponification of potassium ethyl malonate. With the di-ethyl malonate and one equivalent of caustic soda, practically the same rate was obtained. In solutions as concentrated as N/10 the constant decreases steadily. This was apparently due to the method of titration. The dissociation constant of the malonic ester is believed to be no larger than that of water. W. D. B.

**The decomposition of carbon monoxide and the blast-furnace equilibrium.** *R. Schenck and F. Zimmermann. Ber. chem. Ges. Berlin, 36, 1231, 3663 (1903).* — The metals, cobalt, nickel and iron, accelerate the decomposition of carbon monoxide into carbon dioxide and carbon while the oxides do not. At higher temperatures the reaction is a bimolecular one,



At lower temperatures the reaction is monomolecular and the authors assume two stages



The order of the reaction at any given temperature may vary with the catalytic agent, being monomolecular at 445° with iron and bimolecular with nickel. The calculations are made on the basis of a reaction running to an end, a condition which is not fulfilled in this case.

Since iron is oxidized by carbon dioxide, the final products with an excess of iron are carbon, iron and oxide of iron, the gas pressure becoming approximately zero. Mercury acts as a catalytic agent for the reaction between iron and carbon dioxide. W. D. B.

**The decomposition of antimony hydride.** *A. Stock and O. Guttman. Ber. chem. Ges. Berlin, 37, 901 (1904).* — The decomposition of antimony



hydride takes place at ordinary temperatures and can be followed by pressure measurements. The results confirm the theory that antimony acts as a catalytic agent, the reaction taking place with relatively high velocity at the surface of the antimony. The catalytic action of the antimony varies with the nature of the deposit.  
W. D. B.

Remarks on the paper of Messrs. Stock and Guttman on the catalytic decomposition of antimony hydride. *M. Bodenstein. Zeit. phys. Chem.* 37, 1361 (1904). — The author calculates the results of Stock and Guttman (preceding review) and shows that they agree well with the formula for a monomolecular reaction with antimony as catalytic agent.  
W. D. B.

The kinetics of oxidation with permanganate. *N. Schilow. Ber. chem. Ges. Berlin*, 36, 2735 (1903). — It is believed that the reaction between permanganate and oxalic acid takes place according to the following scheme :

$\text{Mn(OH)}_7 + 2(\text{COOH})_2 = \text{Mn(OH)}_3 + 4\text{CO}_2 + 4\text{H}_2\text{O}$ , very slowly  
 $\text{Mn(OH)}_7 + \text{Mn(OH)}_2(\text{CO}_2\text{H})_2 = \text{Mn(OH)}_6 + \text{Mn(OH)}_2(\text{COOH})_2$ , measurable

$\text{Mn(OH)}_2(\text{COOH})_2 + \text{Mn(OH)}_6 = \text{Mn(OH)}_3 + 4\text{CO}_2 + 4\text{H}_2\text{O}$ , instantaneous.  
 $\text{Mn(OH)}_3 + 2(\text{COOH})_2 = \text{Mn(OH)}_2(\text{COOH})_2$ , instantaneous.

With formic acid manganese dioxide is formed and the reaction stops. A mixture of formic and oxalic acids reduces permanganate faster than either alone.  
W. D. B.

More on the autoxidation of cerous salts. *E. Baur. Ber. chem. Ges. Berlin*, 36, 3038 (1903). — A reply to Engler. The author has repeated his earlier measurements and obtains the same result. It would be better in this and in other cases for each man to make at least one experiment exactly as the other man did, so as to be certain whether it was a question of experimental error only.  
W. D. B.

Active oxygen, IX. *C. Engler. Ber. chem. Ges. Berlin*, 37, 49 (1904). — Baur has disputed the accuracy of the author's statement that one-half the oxygen is made active when a cerous salt is oxidized in aqueous potassium carbonate solution with arsenious acid as acceptor. The experiments have therefore been repeated with great care and the previous results confirmed.  
W. D. B.

New experiments on the oxygen absorption in alkaline cerous solutions. *E. Baur. Ber. chem. Ges. Berlin*, 37, 795 (1904). — Experiments showed that the percentage absorption of oxygen varies with different samples of cerous salts and also with the degree of alkalinity of the solution. With one sample of cerous chloride the author obtained the following absorptions expressed in percentage of peroxide formed : 52.3, 44.2, 37.2, 51.2, 52.3, 55, 44, 52.3. With the same salt, but another solution, the values were : 60.1, 75.9, 67.8, 59.3, 76.3, 62.8.  
W. D. B.

The preparation of potassium platinumous chloride. *P. Klason. Ber. chem. Ges. Berlin*, 37, 1360 (1904). — The reaction between potassium platinumous chloride and potassium oxalate does not take place when the platinum salt is pure. There must be a trace of iridium salt present to act as catalytic agent.  
W. D. B.

*Electrolysis and Electrolytic Dissociation.*

**Electrolysis of fused organic salts.** *E. Berl. Ber. chem. Ges. Berlin*, 37, 325 (1904). — Lassar-Cohn found that methane and hydrogen are set free at the cathode when fused potassium acetate is electrolyzed. The author shows that this is due to the action of metallic potassium on the fused acetate. When fused lead acetate is electrolyzed with a mercury cathode, lead alone is formed at the cathode and carbon dioxide at the anode. Other products are formed in the melt but have not been investigated. *W. D. B.*

**Electrolytic determination of antimony and the separation from tin.** *A. Fischer. Ber. chem. Ges. Berlin*, 36, 2348 (1903). — Potassium cyanide decomposes sodium polysulphide and thereby facilitates the electrolytic precipitation of antimony. A separation of antimony from tin takes place readily when the antimony is present in a trivalent form, but not when it is pentavalent. *W. D. B.*

**Electrolytic separation of silver from antimony.** *A. Fischer. Ber. chem. Ges. Berlin*, 36, 3345 (1903). — Silver can be separated quantitatively from antimony in a nitric acid solution if tartaric acid is added. The tartaric acid keeps up the antimony and also prevents the formation of silver peroxide. After adding caustic soda and sodium monosulphide, the antimony can be deposited quantitatively. A separation can also be effected in cyanide solution provided the antimony is present in the pentavalent form. *W. D. B.*

**Electrolytic separation of manganese and iron.** *J. Köster. Ber. chem. Ges. Berlin*, 36, 2716 (1903). — The addition of phosphorous acid to a solution of manganese and iron prevents the precipitation of manganese peroxide at the anode. Care must be taken not to add too much or the iron will not all precipitate at the cathode. *W. D. B.*

**Electrolytic preparation of alkali selenates.** *E. Müller. Ber. chem. Ges. Berlin*, 36, 4262 (1903). — Sodium selenite can easily be oxidized to selenate between platinum electrodes. When no potassium chromate is added there is a slight reduction to metallic selenium at the cathode. *W. D. B.*

**The decomposition of hydrogen peroxide by electrolytic oxygen and hydrogen.** *S. Tanatar. Ber. chem. Ges. Berlin*, 36, 199 (1903). — Electrolytic oxygen oxidizes hydrogen peroxide to water and oxygen; electrolytic hydrogen reduces it to water. The efficiency is greater the more concentrated the hydrogen peroxide and the lower the current density. Concentrated sulphuric acid exerts a protecting influence. *W. D. B.*

**The electrochemical behavior of radium.** *A. Coehn. Ber. chem. Ges. Berlin*, 37, 811 (1904). — When a radium barium bromide solution in alcohol, acetone or pyridine is electrolyzed between platinum electrodes, both electrodes become radio-active; but this soon disappears, showing that it was only an induced activity. In aqueous solutions with mercury or amalgamated zinc cathodes, the radium precipitates before the barium; but the relative concentrations are such that it is impossible to effect a separation. Neither barium nor

radium will precipitate in a cathode of fused Wood's alloy. A methyl alcohol solution is better for the amalgam formation than an aqueous solution.

W. D. B.

**Nitromethane as solvent.** *L. Bruner. Ber. chem. Ges. Berlin, 36, 3297 (1903).* — The dielectric constant of nitromethane is 56.4 and the specific conductivity at 18° is about  $6.4 \times 10^{-7}$  reciprocal ohms. Tribromacetic acid, antimony trichloride, antimony tribromide and mercuric chloride show a slight conductivity in nitromethane solutions. Tribromacetic acid in trichlor-nitromethane showed no measurable conductivity.

W. D. B.

**The amphoteric character of cacodylic acid.** *J. v. Zawidski. Ber. chem. Ges. Berlin, 36, 3325 (1903).* — The author concludes that cacodylic acid is an extraordinarily weak acid, but that strong bases form with it salts which show practically no hydrolysis. This would make it a pseudo-acid. Since it is also an amphoteric electrolyte, the author concludes that the supposed characteristics of pseudo-acids are not limited to these but may occur with amphoteric electrolytes.

W. D. B.

**Note on amphoteric electrolytes and especially on cacodylic acid.** *A. Hantzsch. Ber. chem. Ges. Berlin, 37, 1076 (1904).* — Zawidski classed the sodium cacodylate as abnormal because its hydrolysis was not of the same order as that of sodium carbonate. The author points out that the comparison should be made with primary sodium carbonate, in which case there is nothing abnormal. This disposes of v. Zawidski's assumption that "the absence of hydrolysis in the alkali salts of acids which scarcely conduct may occur with amphoteric electrolytes as well as with pseudo-acids."

W. D. B.

**On complex silver ions.** *H. Euler. Ber. chem. Ges. Berlin, 36, 2878 (1903).* — The solubility of silver chloride in methylamine and ethylamine solutions is proportional to the concentration of the base. The complex cations have the composition  $\text{Ag}(\text{CH}_3\text{NH}_2)_2^+$  and  $\text{Ag}(\text{C}_2\text{H}_5\text{NH}_2)_2^+$ , corresponding to  $\text{Ag}(\text{NH}_3)_2^+$ .

W. D. B.

**The composition of the silver compounds in solutions of methyl and ethyl amine.** *G. Bodländer and W. Eberlein. Ber. chem. Ges. Berlin, 36, 3945 (1903).* — Solubility determinations and electromotive force measurements show that silver chloride dissolves in methylamine and ethylamine solutions, forming the complex cations  $\text{Ag}(\text{CH}_3\text{NH}_2)_2^+$  and  $\text{Ag}(\text{C}_2\text{H}_5\text{NH}_2)_2^+$ , as was also found by Euler (preceding review).

W. D. B.

**The metal-ammonia hydroxides.** *W. Bonsdorff. Ber. chem. Ges. Berlin, 36, 2322 (1903).* — With zinc ammonia hydroxide it was shown that zinc moved to the cathode only. Electromotive force measurements make it probable that the complex cation has the formula  $\text{Zn}(\text{NH}_3)_3^{++}$ . With cadmium the complex cation has the formula  $\text{Cd}(\text{NH}_3)_4^{++}$ . Measurements have also been made on the conductivity, the solubility and the catalytic action upon diacetone alcohol for the ammoniacal solutions of zinc, cadmium, nickel, copper and silver.

W. D. B.

**Complex ions of zinc and cadmium.** *H. Euler. Ber. chem. Ges. Berlin,*

36, 3400 (1903). — The author has determined the solubility of zinc and cadmium hydroxides in aqueous ammonia and has also made electromotive force measurements with solutions of zinc and cadmium hydroxides in aqueous ammonia and with solutions of zinc and cadmium cyanides in potassium cyanide solutions. In the ammoniacal solutions we have the complex cations  $\text{Zn}(\text{NH}_3)_4^{++}$  and  $\text{Cd}(\text{NH}_3)_4^{++}$ , the first being one hundred times as stable as the second. In the cyanide solutions we have the complex anions  $\text{Zn}(\text{CN})_4^{--}$  and  $\text{Cd}(\text{CN})_4^{--}$ , the two being about equally stable. On the basis of these and other measurements, the author criticizes Abegg's theory of valence. *W. D. B.*

The formation of complexes. *R. Abegg. Ber. chem. Ges. Berlin, 36, 3684 (1903).* — This is a reply to the criticisms by Euler (preceding review). *W. D. B.*

On some complex metal compounds. *G. Bodländer. Ber. chem. Ges. Berlin, 36, 3933 (1903).* — A table is given showing the formula, limits of concentration, stability constant and energy of formation in calories for sixteen anions of gold, silver, mercury, copper and zinc. In yet another table is given the potential differences between solutions containing these complex ions and the corresponding metal. There is also a reply to Euler (two reviews back). *W. D. B.*

#### Dielectricity and Optics

The combustion of nitrogen to nitric oxide in the electric flame. *W. Muthmann and H. Hofer. Ber. chem. Ges. Berlin, 36, 438 (1903).* — The authors look upon the electric arc purely as a means of getting a high temperature. They believe that an equilibrium is reached between nitrogen and its oxides, and that the sudden chilling in the surrounding air prevents the reaction from going back. They get a better yield of oxides of nitrogen, the higher the temperature. The waste of heat is in raising the temperature of the surrounding air. The reaction is written



Although compressed air gave much better results than air under atmospheric pressure, the authors do not feel very sanguine as to the immediate commercial success of nitrates from the air. *W. D. B.*

The oxidation of atmospheric nitrogen by electrical discharges. *F. v. Lepel. Ber. chem. Ges. Berlin, 36, 1251 (1903).* — The author works with a direct current and a so-called aureole discharge. The oxidation to NO takes place essentially in the flame, the further oxidation to nitrogen dioxide outside the flame. The nature of the electrodes has a marked effect, though it is not yet possible to make any generalization. *W. D. B.*

Relation between arc, temperature and yield of oxides of nitrogen by electrical discharges in air. *F. v. Lepel. Ber. chem. Ges. Berlin, 37, 712 (1904).* — More oxides of nitrogen are formed at the anode than at the cathode. A mean temperature for the air is best. Rotating the anode is not advantageous. With stationary anode, the yield increases with increasing length of arc, but this is not the case with a rotating anode. Impregnation of the cathode with titanium chloride is beneficial. *W. D. B.*

**The formation of ozone.** *E. Goldstein. Ber. chem. Ges. Berlin, 36, 3042 (1903).* — When the spark from an induction coil passes inside a quartz tube in which the pressure has been reduced to about a millimeter, there is a marked formation of ozone outside the tube. This is undoubtedly due to the action of ultra-violet light passing through the walls of the tube. When oxygen under about a millimeter pressure is passed between the poles of an induction coil and is cooled to the temperature of liquid air, there is a quantitative yield of ozone.

W. D. B.

**On radium.** *W. Marckwald. Ber. chem. Ges. Berlin, 37, 88 (1904).* — When a barium-radium chloride solution is shaken with a one percent sodium amalgam, the ratio of radium to barium in the resulting amalgam is greater than in the original solution.

The anhydrous chlorides phosphoresce while the hydrated chlorides do not. Experiments with radio-tellurium, which emits  $\alpha$ -rays only, and with the  $\beta$ -rays from the radium enclosed in an aluminum capsule show that the anhydrous chlorides phosphoresce under the influence of the  $\alpha$ - and  $\beta$ -rays, while the hydrated chlorides do not.

Some experiments with weak radium solutions seem to show that the amount of activity induced in other metals depends on the position of the metal in the voltaic series.

W. D. B.

**Radio-active lead as a primary active substance.** *K. Hofman and V. Wölfl. Ber. chem. Ges. Berlin, 36, 1040 (1903).* — "There exists a substance which can be separated from ordinary inactive lead, though like it in most analytical reactions. This substance shows very strong primary activity, sending out  $\alpha$ - and  $\beta$ -rays and inducing strong activity in other metals whether these are exposed as metals or as dissolved salts."

W. D. B.

**Light-sensitive solutions of lead salts.** *K. A. Hofmann and V. Wölfl. Ber. chem. Ges. Berlin, 37, 249 (1904).* — When a dilute solution of a lead halide in aqueous sodium thiosulphate is exposed to sunlight, there are formed red crystals which seem to be polysulphides of the lead halides. For the iodide compound, the formula  $\text{IPb}_2\text{S}_3 \cdot \text{PbI}_2$  is suggested, or  $\text{PbI}_4 \cdot 2\text{PbS}_2$ . The chloride compound is apparently  $\text{PbCl}_2 \cdot 3\text{PbS}_2$ . The shorter light waves are more effective than the longer ones. In diffused light black lead sulphide alone is formed.

W. D. B.

**The action of cathode rays on inorganic and organic substances.** *E. Goldstein. Ber. chem. Ges. Berlin, 36, 1876 (1903).* — Ammonium chloride is not colored by the cathode rays at ordinary temperatures, but is at lower temperatures. Very many halogen-substituted substances are colored by the cathode rays at very low temperatures. Since sulphur is also affected, the author believes that we have in all cases to deal with an allotropic change. This conclusion would be more convincing if there were any certainty that the sulphur used did not contain sulphur dioxide. Under the influence of the cathode rays, frozen sulphuric acid becomes temporarily yellow, hydrochloric acid and hydrobromic acid green.

W. D. B.

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==THE==  
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## THE RATE OF THE REACTION BETWEEN IODIC AND HYDRIODIC ACIDS

BY SAUL DUSHMAN

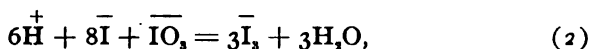
In 1888 the rate of reaction between iodic and hydriodic acids was made the subject of a research by O. Burchard,<sup>1</sup> who endeavored to discover a relation between the rate and the concentrations of these two reagents. His results, however, were unsatisfactory, and the author concludes his paper with the words, "In spite of all attempts, I have not succeeded in representing the rate of the reaction by a general differential equation".

In light of the electrolytic dissociation theory introduced by Arrhenius just at the time of Burchard's publication, it now seems advisable to represent hydrogen iodide in solution as consisting almost entirely of hydrion ( $\text{H}^+$ ) and iodion ( $\text{I}^-$ ); similarly a solution of iodic acid contains hydrion ( $\text{H}^+$ ) and iodation ( $\text{IO}_3^-$ ), while brown "iodine" solution contains tri-iodion ( $\text{I}_3^-$ ).

Thus, in place of Burchard's equation,



it seems better to write



and in consequence, I have studied the effect of the concentrations of  $\text{H}^+$ ,  $\text{I}^-$ ,  $\text{IO}_3^-$  and  $\text{I}_3^-$  on the rate, instead of adopting the variables chosen by Burchard.

In planning the experiments, I adopted a method which was originally employed by Harcourt and Esson in their classical research, "On the Observation of the Course of Chemical Change", in 1866,<sup>2</sup> but which had, apparently been completely forgotten by 1888. The principle of the method is very sim-

<sup>1</sup> Zeit. phys. Chem. 2, 796 (1888).

<sup>2</sup> Jour. Chem. Soc. 20, 476 (1867).

ple, and consists in keeping the concentrations of all the reagents but one constant, or almost constant, during the progress of the reaction; any change in the rate must then be ascribed to changes in the concentration of that one substance only. In Burchard's work on the other hand, the concentrations of all the reagents changed during every experiment, and he was unable to discover the effect due to each.

In the investigations of Harcourt and Essen, and in those carried on in this laboratory by Messrs. Bray,<sup>1</sup> Bell,<sup>2</sup> Roebuck,<sup>3</sup> DeLury,<sup>4</sup> Forster,<sup>5</sup> and Miss Benson,<sup>6</sup> the concentrations of all the reagents except one were *held constant by employing relatively high concentrations of the reagents in question*. In my preliminary experiments I made up the solutions on the same plan, using a small amount of potassium iodate (iodation), and large excesses of potassium iodide (iodion) and hydrochloric acid (hydrion). I soon found, however, that the solutions had to be much diluted in order to make the rate of the reaction slow enough to measure, and that in these very dilute solutions accurate analytical determination of the iodine liberated was impossible.

Finally I replaced the excess of hydrochloric acid by excess of acetic acid and sodium acetate, thus obtaining solutions in which *the concentration of the hydrion, though lower than those of the iodation and iodion, remained unaltered* throughout the experiment. In the acetic acid solutions the rate was much slower than in those containing hydrochloric acid, great dilution was not necessary, and the analytical difficulties referred to above were avoided.

Experiments in which the concentrations of the reagents were systematically varied led to very simple results, namely, that the rate of the reaction between hydriodic and iodic acids

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<sup>1</sup> Jour. Phys. Chem. 7, 92 (1903).

<sup>2</sup> Ibid. 7, 61 (1903).

<sup>3</sup> Ibid. 6, 365 (1902).

<sup>4</sup> Ibid. 7, 239 (1903).

<sup>5</sup> Ibid. 7, 640 (1903).

<sup>6</sup> Ibid. 7, 1 (1903).

is proportional to the concentration of the iodation, to the square of the concentration of the hydrion, and to the 1.8th or 1.9th power of that of the iodion, while the tri-iodion exerts an accelerating influence which was studied in detail. By means of the differential equation embodying these relations, I was able to predict the course of the reaction in solutions containing hydriodic and iodic acids only.

The results, apart from their intrinsic interest, are of value as showing the power of Harcourt and Esson's method in the study of Chemical Kinetics. As recently as 1898, in a paper on "The Reduction of Bromic Acid and the Law of Mass Action",<sup>1</sup> the authors, Messrs. Judson and Walker, expressed themselves as follows: "It is evident, therefore, that the action of hydriodic acid on the oxygen acids of the halogens is of too intricate a nature to give any satisfactory numerical results". The rate of this "intricate reaction" is now known as a simple function of the concentrations of the reagents involved.

### METHOD OF WORKING

#### Precautions taken to exclude air

As the unsatisfactory outcome of Burchard's investigation has been ascribed in part to the action of atmospheric oxygen on his solutions, I took special precautions to exclude air during the work. Pairs of experiments, however, in one of which the air was excluded, while in the other it was allowed access, seemed to show that the error arising from this source was negligible.

All the solutions used in the experiments were prepared free from air by boiling and cooling in vacuo, and were kept under carbonic acid gas, which was purified by passing through water, solutions of sulphuric acid, ferrous sulphate, and permanganate of potassium, and through a long tube filled with cotton wool.

Before removing a solution from one of the stoppered flasks clamped in the thermostat (see below), the pipettes were filled

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<sup>1</sup> Jour. Chem. Soc. 73, 411 (1898).

with carbon dioxide, and a current of the gas was passed into the flask as long as the stopper was out.

#### **Description of an experiment**

The main stock of the solutions of potassium iodide, potassium iodate, acetic acid and sodium acetate was kept in bottles under carbon dioxide, as already stated; and before each series of experiments about 200 cc of each were brought to 0° C in stoppered flasks (clamped in the thermostat) from which the air had been removed by a current of carbon dioxide. The thermostat was also provided with a large test-tube (100 cc capacity) and a 500 cc beaker with stirring rod.

Each measurement contained in the following tables involved the preparation of a new reacting mixture, as follows: Into the test-tube was first pipetted air-free water in quantity sufficient (together with that of the reagents subsequently added) to make up the total volume to 100 cc; measured quantities of sodium acetate, acetic acid and potassium iodide solutions were then added. The potassium iodate was measured into the beaker and the stirrer set in motion, the contents of the test-tube were then thrown in, and at the same instant the catch of a stop-watch was released by means of a pedal. Experiments with colored solutions showed that a homogeneous mixture was attained in from one-fifth to one-half second. When it was desired to interrupt the reaction, the contents of the beaker were again stirred rapidly, about 10 cc of ammonium bicarbonate solution thrown in from a test-tube and the watch stopped. The iodine liberated was then determined with centinormal sodium arsenite and iodine solutions, using starch as an indicator.<sup>1</sup> Duplicate experiments gave results agreeing within 0.10 cc of the volumetric arsenite solution, while duplicate analyses of the same mixture agreed within 0.05 cc.

All pipettes and burettes used in these measurements were freshly calibrated, the pipettes by weighing the distilled water discharged at 4° C, and the burettes as described in Ostwald's

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<sup>1</sup> For the method of analysis of the mixture in presence of excess of iodine, see page 468.

"Hand- und Hilfsbuch," page 103. In using the pipettes 45 seconds were allowed for draining.

#### Solutions employed

*Water.* — All the water used in these experiments was freed from air, and kept under carbon dioxide.

*Potassium iodate.* — 0.00918-F,<sup>1</sup> and 0.00100-F  $\text{KIO}_3$ , prepared by dissolving weighed quantities of the salt, and standardized by decomposing a measured volume with excess of potassium iodide and hydrochloric acid, adding excess of ammonium bicarbonate, and titrating with 0.01049-*n* sodium arsenite.

*Sodium acetate.* — 0.10035-F,  $\text{C}_2\text{H}_3\text{O}_2\text{Na}$ , prepared by dissolving 13.6 grams of Merck's crystallized sodium acetate to one liter; a few crystals of menthol were added to prevent the growth of moulds. To standardize it, a measured volume was evaporated in a tared crucible at 100° C, the crucible and salt were then heated to 110°–120° for four hours, allowed to cool in a desiccator, and the anhydrous sodium acetate weighed.

*Acetic acid.* — 1.147-F,  $\text{C}_2\text{H}_4\text{O}_2$ , prepared by diluting Merck's "pure glacial acetic acid, 99.5 percent acid", and titrating against standard potash.

*Hydriodic acid.* — 0.1128-F and 0.001132-F HI; prepared by diluting a stock solution made from water, iodine, and red phosphorus; titrated against the standard potash. These solutions contained a little free iodine, which was determined by sodium arsenite (20 cc of the 0.1128-F HI took 0.42 cc of 0.0105-*n* arsenite), and in each measurement in which hydriodic acid was used, the small correction for the free iodine was made at the time of the analysis.

*Iodic acid.* — 0.00976-F and 0.00100-F  $\text{HIO}_3$ . Large, colorless crystals of iodic acid, free from sulphuric acid (prepared by oxidizing iodine with nitric acid, sp. gr. 1.53) were dissolved, and the solutions standardized by sodium arsenite (see under Potassium iodate).

*Iodine and potassium iodide.* — Twenty-five cc was equiva-

<sup>1</sup> Formula-weights per liter.



lent to 21.77 cc 0.1049-N arsenite, hence 0.04567-F tri-iodion,  $I_3^-$ . After boiling off the free iodine, 50 cc with silver nitrate gave 1.1387 g AgI, hence 0.0970-F KI. Since each mol of iodine ( $I_2$ ) reacts with one of potassium iodide (iodion,  $I^-$ ) to form one of potassium tri-iodide (tri-iodion,  $I_3^-$ ) the formation of 0.04567 mol  $I_3^-$  per liter has used up 0.04567 mol iodion, leaving 0.0970 — 0.04567 = 0.05133 mol iodion ( $I^-$ ) per liter.

*Iodine and hydriodic acid.*—The 0.1128-F hydriodic acid was saturated with iodine, and the "free iodine" (tri-iodion) determined by sodium arsenite and found to be 0.0415-F  $I_3^-$ . Subtracting 0.0415 from 0.1128 there remains the concentration of the iodion, 0.0713-F, while the hydrion is 0.1128-F  $H^+$ .

*Volumetric sodium arsenite.*—0.01049-normal; standardized with dry, freshly sublimed iodine. The *volumetric iodine solutions* were compared daily with the arsenite; and the *volumetric sodium thiosulphate* was standardized against the iodine solutions.

The half saturated *ammonium bicarbonate* solution was kept under  $CO_2$ . A distinct blue coloration was obtained when one drop of centinormal iodine was added to a mixture of 100 cc water, 10 cc ammonium bicarbonate solution, 2 cc starch solution, and a few drops of normal potassium iodide.

## RESULTS OF THE EXPERIMENTS

### Explanation of the Tables (Series I and II)

At the head of each table is given the initial composition of the reacting mixture. The numbers following each formula denote the number of gram-formula-weights of that reagent in 100 cc of reacting mixture. Thus  $IO_3^-$ , 0.000025;  $I^-$ , 0.00177; HAc, 0.00585; NaAc, 0.0015 (at the head of Table 1) means that 25 cc of 0.0010-F  $KIO_3$ , 20 cc of 0.0885-F KI, 5 cc of 1.17-F HAc, 15 cc of F/10 NaAc were made up to a volume of 100 cc. From the numbers after HAc and NaAc, was calculated the quantity of hydrion,  $H^+$ , in the mixture, assuming the dissocia-

tion constant of acetic acid to be 0.000018,<sup>1</sup> and the sodium acetate to be totally dissociated; thus for HAc 0.00585, and NaAc 0.0015 (V 0.1 liter).

$$KV(\text{HAc}) = \overset{+}{\text{H}} \times \overline{\text{Ac}}$$

$$0.000018 \times 0.1 \times 0.00585 = \overset{+}{\text{H}} \times (\overset{+}{\text{H}} + 0.0015),$$

whence  $\overset{+}{\text{H}} = 0.000007$

Under "*t*" is entered the time in minutes during which the mixture was allowed to react, and under "*As*" the number of cc of the volumetric sodium arsenite equivalent to the iodine liberated. In the third column are entered the values  $k_1$  or  $k_2$ .

$$k_1 = -\frac{1}{t} \log_{10} \frac{IO_3}{IO_3 - x}, \dots\dots\dots (I)$$

$$k_2 = -\frac{1}{t} \left( \frac{1}{I-y} - \frac{1}{I} \right) \dots\dots\dots (II)$$

To obtain  $x$ , the number of mols of  $IO_3$  reduced for each cc of *As*, the burette readings must be multiplied by 0.00000175. (1 cc *As* = 0.00001049 equivalent; 1 mol  $IO_3$  gives 6 equivalents of iodine.)

To obtain  $y$ , the number of mo's of  $\bar{I}$  corresponding to 1 cc of *As* in the titration, the burette readings must be multiplied by 0.00001398. (From equation (2)

8 KI yields 3  $KI_3$  = 6 equivalents of iodine,  
or for each mol of KI destroyed, 3/8 mol. of  $KI_3$  is formed,  
that is, 3/4 equivalent of *As* is used in titration. Hence, 1 cc *As* =  $4/3 \times 1/1000 \times 0.01049 = 0.00001398$  mol KI.)

#### SERIES I. ACETIC ACID SOLUTIONS, POTASSIUM IODATE PRESENT IN SMALL QUANTITY

##### Effect of Iodation

The constancy of  $k_1$  in each of the tables of this series shows that the rate is proportional to the concentration of the potassium iodate (iodation) in the reacting mixture. This conclusion is confirmed by the fact that doubling the concentration

<sup>1</sup> From the data and formulas of Arrhenius' paper (Zeit. phys. Chem. 4, 106) it appears that at 0° C the dissociation constant of acetic acid is below 0.000017. The hydron concentrations given at the heads of Tables 1-27 are therefore all somewhat too high. See, however, page 474.

of the iodate does not affect  $k_1$  (Tables 2 and 1). The slight falling off of  $k_1$  in Table 2 is to be expected, as the concentration of the iodide is in relatively small excess.

#### Effect of Hydrion

From a comparison of Tables 1 and 3, and 1 and 4, it is apparent that the rate is proportional to the square of the concentration of the hydrion. In the first pair, the concentration of the hydrion was changed by doubling the concentration of the acetic acid, and in the second pair by doubling that of the sodium acetate. In Table 5 the concentration of both acid and salt is double that in Table 1, but the rate remains the same, thus affording a striking confirmation of the view that it is the concentration of hydrion that is effective.

#### Effect of Iodion

The effect of the concentration of iodion is not quite so simple. From Tables 1 and 6, 7 and 4, it is seen that doubling the concentration of the potassium iodide (iodion) multiplies the rate by  $2^{1.85}$  or  $2^{1.9}$ . From Tables 9 and 10 we see that varying the concentration of iodion from 0.00886 to 0.000886 mol per liter, does not cause any variation in the exponent. It can, however, be seen from Table 10, and it will be more apparent from Series II, that the lower the concentration of iodion, the nearer the proportionality is between the rate and the square of its concentration. The other tables of this series show that the effects of the acid, acetate, and iodide are each independent of the others as well as of the iodate.

TABLE I

$\text{IO}_3$ , 0.000025; I, 0.00177; HAc, 0.00585; NaAc, 0.0015;  
H, 0.0000070

$t$	$As$	$k_1 \times 10^3$
2	1.13	17.9
4	2.24	18.5
6	3.15	18.0
8	4.15	18.6
10	4.87	18.6
		Av. 18.3

TABLE 2

$\text{IO}_3$ , 0.000050 ; I, 0.00177 ; HAc, 0.00585 ; NaAc, 0.0015 ;  
H, 0.000007

$t$	$As$	$k_1 \times 10^3$
2	2.20	17.4
2	2.26	17.9
4	4.04	16.8
6	6.09	17.3
8	7.24	15.8
		Av. 17.3

TABLE 3

$\text{IO}_3$ , 0.000025 ; I, 0.00177 ; HAc, 0.0117 ; NaAc, 0.0015 ;  
H, 0.000014

$t$	$As$	$k_1 \times 10^3$
1	2.30	76.2
2	4.17	75.0
2	4.14	74.4
2.5	4.78	71.0
4	6.87	71.2
6	8.76	68.7
		Av. 72.6

TABLE 4

$\text{IO}_3$ , 0.000025 ; I, 0.00177 ; HAc, 0.00585 ; NaAc, 0.0030 ;  
H, 0.0000035

$t$	$As$	$k_1 \times 10^3$
2	0.34	5.3
4	0.62	4.8
6	0.89	4.7
8.5	1.22	4.6
10	1.54	4.9
		Av. 4.8

TABLE 5

$\text{IO}_3$ , 0.000025 ; I, 0.00177 ; HAc, 0.0117 ; NaAc, 0.0030 ;  
H, 0.000007

$t$	$As$	$k_1 \times 10^3$
2	1.22	19.4
4	2.27	18.8
6	3.21	18.4
8	4.35	19.7
		Av. 19.1

TABLE 6

$\text{IO}_3$ , 0.000025 ; I, 0.00354 ; HAc, 0.00585 ; NaAc, 0.0015 ;  
H, 0.000007

$t$	$As$	$k_1 \times 10^3$
2	3.86	68.4
3	5.16	64.8
4	6.50	65.9
6	8.18	61.5
8	9.62	60.7
		Av. 64.3

TABLE 7

$\text{IO}_3$ , 0.000025 ; I, 0.00354 ; HAc, 0.00585 ; NaAc, 0.0030 ;  
H, 0.0000035

$t$	$As$	$k_1 \times 10^3$
2	1.17	18.5
4	2.19	18.1
6	3.20	18.3
8	3.93	17.5
10	4.78	17.6
		Av. 18.0

TABLE 8

$\text{IO}_3$ , 0.000025; I, 0.00354; HAc, 0.0117; NaAc, 0.0015;  
H, 0.000014

$t$	$As$	$k_1 \times 10^3$
1	6.03	236.0
1.5	7.96	235.8
1.75	8.89	241.5
2	9.54	239.0
		Av. 238.2

TABLE 9

$\text{IO}_3$ , 0.000025; I, 0.00885; HAc, 0.00585; NaAc, 0.0015;  
H, 0.000007

$t$	$As$	$k_1 \times 10^3$
1	8.64	403.2
1.25	9.66	391.5
1.50	10.46	381.2
1.75	11.24	383.4
		Av. 389.8

TABLE 10

$\text{IO}_3$ , 0.000025; I, 0.000885; HAc, 0.00585; NaAc, 0.0015;  
H, 0.000007

$t$	$As$	$k_1 \times 10^3$
2	0.32	4.9
4	0.57	4.4
6	0.96	5.0
8	1.25	5.0
10	1.45	4.6
		Av. 4.8

**SERIES II. ACETIC ACID SOLUTIONS, POTASSIUM IODIDE  
PRESENT IN SMALL QUANTITY**

**Effect of Iodion**

The constancy of  $k_2$  in each of the tables of this series shows that the effect of iodion varies as the square of its concentration when it is present in small quantity relatively to the iodate. In confirmation of this conclusion, we find that Table 12, in which the concentration of the iodide (iodion) is doubled, gives approximately the same constant as Table 11.

**Effect of Iodation**

Table 13 shows that doubling the concentration of the potassium iodate (iodation) multiplies the rate by 2; hence, as in Series I, the rate varies with the first power of the concentration of the iodation.

**Effect of Hydrion**

Tables 11 and 14, and 11 and 15, show that halving or doubling the concentration of the hydrion multiplies the rate by  $\frac{1}{4}$  or 4 respectively. Tables 11 and 16 show that if the concentration of both acid and acetate be doubled, the rate remains unchanged. Hence, as in Series I, the rate is proportional to the second power of the concentration of the hydrion.

TABLE 11  
IO<sub>3</sub>, 0.000225; I, 0.00018; HAc, 0.0117; NaAc, 0.0015;  
H, 0.000014

$t$	$As$	$k_2$
4	1.06	125
6	1.46	120
8	1.84	116
12	2.69	122
15	3.07	116
		—
		Av. 120

TABLE 12

IO<sub>3</sub>, 0.000225 ; I, 0.00036 ; HAc, 0.0117 ; NaAc, 0.0015 ;  
H, 0.000014

<i>t</i>	<i>As</i>	<i>k<sub>1</sub></i>
1	1.04	119
2	1.86	109
3	2.72	110
4	3.46	108
		—
		Av 112

TABLE 13

IO<sub>3</sub>, 0.00045 ; I, 0.00018 ; HAc, 0.0117 ; NaAc, 0.0015 ;  
H, 0.000014

<i>t</i>	<i>As</i>	<i>k<sub>1</sub></i>
2	0.99	232
3	1.44	233
4	1.92	241
6	2.60	234
8	3.14	227
		—
		Av. 235

TABLE 14

IO<sub>3</sub>, 0.000225 ; I, 0.00018 ; HAc, 0.0117 ; NaAc, 0.0030 ;  
H, 0.000007

<i>t</i>	<i>As</i>	<i>k<sub>1</sub></i>
16	1.10	33
24	1.45	29
		—
		Av. 31



TABLE 15

$IO_3$ , 0.000225 ;  $I$ , 0.00018 ;  $HAc$ , 0.0234 ;  $NaAc$ , 0.0015 ;  
 $H$ , 0.000028

$t$	$As$	$k_2$
2	1.64	406
3	2.43	452
4	3.05	432
		Av. 442

TABLE 16

$IO_3$ , 0.000225 ;  $I$ , 0.00018 ;  $HAc$ , 0.0234 ;  $NaAc$ , 0.0030 ;  
 $H$ , 0.000007

$t$	$As$	$k_2$
4	1.10	130
6	1.45	120
8	1.73	108
12	2.58	112
		Av. 117

#### Representation of the results by a differential equation

The results of the measurements of Series I and II may thus be stated in the following words :

"The rate of the reaction between iodation, iodion, and hydron, is proportional to the first power of the concentration of the iodation, to the 1.85th to second power of that of the iodion, and to the second power of the concentration of the hydron."

Or, expressed in the form of a differential equation,

$$\frac{dx}{dt} = K \left( \frac{IO_3 - x}{V} \right) \left( \frac{I - y}{V} \right)^{1.8} \left( \frac{H}{V} \right)^2 \dots\dots\dots (A)$$

where  $y = 8x$ , and  $V$  is the volume in liters.

From the definitions of  $k_1$  and  $k_2$  on page 19, it follows that

$$K = 2.303 k_1 V^3 (I)^{1.8} (H)^2 \dots\dots\dots (B)$$

$$K = k_2 V^3 (IO_3) (H)^2 \dots\dots\dots (C)$$

The following table contains the value of  $K$  for each of the foregoing tables, calculated by means of equations (B) and (C). Its constancy is a measure of the accuracy of equation (A). Physically interpreted,  $K$  represents the calculated number of mols of iodate that should be reduced in one minute when 1 mol of potassium iodide, 1 mol iodate, and 1 mol hydriodic acid were present in a volume of 1 liter.

TABLE 17

No.	$IO_3 \times 10^6$	$I \times 10^6$	$H \times 10^6$	$2303 k_1$	$k_2$	$K \times 10^{-10}$
1	25	177	7.0	42	—	2.47
2	50	177	7.0	39	—	2.30
3	25	177	14.0	167	—	2.46
4	25	177	3.5	11	—	2.59
5	25	177	7.0	44	—	2.59
6	25	354	7.0	138	—	2.34
7	25	354	3.5	41	—	2.59
8	25	354	14.0	548	—	2.12
9	25	885	7.0	896	—	2.47
10	25	89	7.0	11	—	2.59
11	225	18	14.0	—	120	2.73
12	225	36	14.0	—	112	2.56
13	450	18	14.0	—	235	2.70
14	225	18	7.0	—	31	2.82
15	225	18	28.0	—	442	2.55
16	225	18	14.0	—	117	2.68

Av. 2.54

### SERIES III. ACETIC ACID SOLUTIONS, IODINE (TRI-IODION) PRESENT IN EXCESS

It is obvious, that owing to the excess of iodine put into the reacting mixture, it was not possible to make up solutions in which the quantity of potassium iodide was relatively small. Consequently in all the experiments of the present series the potassium iodate was selected as the substance to be present in small quantity.

In the measurements of this series a measured volume of decinormal iodine solution was mixed with the potassium iodate in the beaker (see "Description of an experiment," p. 456), and

water was added to bring the total volume up to 100 cc. Owing to the fact that the iodine liberated during the reaction was very small in amount compared with that initially present, the progress of the reaction was followed by estimating the residual potassium iodate instead of by trying to determine the small increase in the free iodine. The method has been worked out by Mr. Forster.<sup>1</sup>

#### Method of Analysis

The reaction was stopped by throwing in the ammonium bicarbonate, as before; sodium arsenite solution (0.1049*N*) was run in from a burette, and then a little starch solution to determine the end-point. Thrice normal hydrochloric acid was next added in quantity sufficient to neutralize the sodium acetate, the ammonium bicarbonate, and the volumetric sodium arsenite, and to leave an excess of 2 cc of the 3*N* hydrochloric acid. In solutions of this degree of acidity the potassium iodate was immediately reduced with liberation of an equivalent quantity of iodine, which was then determined by 0.01054*N* sodium thio-sulphate.

Blank experiments showed that the results are accurate within 0.10 cc (two drops of the volumetric sodium thiosulphate solution), but it is necessary to complete the titration within five minutes or iodine will be liberated by the action of the arsenic acid formed from the volumetric arsenite.

#### Explanation of the Tables

The symbols  $\text{IO}_3$ ,  $\text{HAc}$ ,  $\text{NaAc}$ ,  $\text{H}$ ,  $\text{I}$ ,  $t$ ,  $k_1$ ,<sup>2</sup> have the meanings assigned on page 458. After  $\text{KI}$  is given the number of mols of potassium iodide, and after "Iod" the number of cc of the iodine solution added in making up the reacting mixture. In the brackets are given the number of mols iodion ( $\bar{\text{I}}$ ) and tri-iodion ( $\bar{\text{I}}_3$ ) contained in the iodine solution. The total quantity of iodion present in the reacting mixture is thus the sum of the

<sup>1</sup> Jour. Phys. Chem. 7, 640.

<sup>2</sup> In the tables of this series  $k_1'$  has been written instead of  $k_1$ , to distinguish the tables of this series from those of Series I.

numbers after KI and I. Under "Th" is given the number of cc of 0.01054-*n* sodium thiosulphate solution equivalent to the iodine liberated from the residual potassium iodate. In order to obtain  $\text{IO}_3 - x$ , used in calculating  $k_i'$ , these burette readings must be multiplied by 0.000001744.

#### Effect of Iodation

From the constancy of  $k_i'$  in each of the tables of this series and by comparing Tables 20 and 23 (in the latter of which the concentration of the potassium iodate was double that in the former) it is apparent that the rate is proportional to the first power of the concentration of the iodation, and that the law according to which the iodation affects the rate is not modified by the presence of tri-iodion.

#### Effect of Hydrion

By comparing Tables 20, 22 and 25 it is evident that the rate is proportional to the square of the concentration of the hydrion. Thus the law according to which the hydrion affects the rate is not modified by the presence of tri-iodion.

#### Effect of Tri-iodion and of Iodion

The effect of tri-iodion might have been determined by comparing the experiments of this series with others in which the composition of the reacting mixture was the same except as regards the tri-iodion. Instead of undertaking a new series of measurements for this purpose, however, I have utilized those of Series I, making a correction for the small difference in the concentration of the iodion by assuming that  $k_i$  is proportional to the 1.9th power of the concentration of the iodion (see page 460). In Table 18 are entered the compositions of the solutions of Tables 19 to 27, and the values of  $k_i'$ ; also under  $k_i$  the constants from the corresponding tables of Series I, corrected as described. The difference  $k_i' - k_i$ , which expresses the effect of tri-iodion on the rate, is roughly proportional to the concentration of the tri-iodion, to somewhat more than the second power of that of the hydrion, and to slightly less than the first power of the iodion.

TABLE 18

No.	$IO^3 \times 10^5$	$I \times 10^6$	$H \times 10^5$	$I_s \times 10^5$	$k_1' \times 10^3$
19	25	2053	7.0	183.0	38.6
20	25	1911	7.0	91.5	27.6
21	25	1841	7.0	45.7	23.6
22	25	1911	14.0	91.5	121.4
23	50	1911	7.0	91.5	29.1
24	25	3682	7.0	91.5	79.5
25	25	1911	3.5	91.5	7.3
26	25	3611	7.0	45.7	72.1
27	25	3820	7.0	183.0	97.2

No.	$k_1 \times 10^3$	$\frac{k_1' - k_1}{\times 10^3}$	$Q$	$k_1' \times 10^3$ calc.	Diff.
19	24.3	14.3	7.8	37.3	— 3.4 %
20	20.8	6.8	7.9	27.3	— 1.1
21	19.8	3.8	9.0	22.9	— 1.7
22	82.8	38.6	(12.5)	108.8	— 10.0
23	19.7	9.4	(10.9)	26.2	— 10.0
24	69.3	10.2	6.2	81.8	+ 4.0
25	5.5	1.8	7.8	7.1	— 3.0
26	66.7	5.4	6.7	72.8	+ 1.0
27	74.3	22.9	6.7	100.3	+ 3.0

Av. 7.4

The quotient,

$$Q = \frac{(k_1' - k_1) V^4 \times 10^{-9}}{(I_s) \times (H)^2 \times (I)},$$

is thus approximately constant, the average value being 7.4. Using this value, I calculate  $k_1'$  for each of the Tables 19 to 27.

$$k_1' \text{ calc} = k_1 + 7.4 \times (I_s) \times (H)^2 \times (I) \times 10^{13} \dots (D)$$

The difference between the calculated and observed values of  $k_1'$  expressed as percent of the latter, is entered under "Diff." With the exception of Tables 22 and 23, the greatest discrepancy is 4 percent, well within the experimental errors. In the case of Tables 22 and 23 the difference amounts to 10 percent;  $k_1'$  for Table 22 is, however, very uncertain (page 472), and if the average of  $k_1'$  for Tables 23 and 20 be entered instead of  $k_1'$  for each of them, the discrepancy between observed and calculated values of  $k_1'$  is reduced to 6 percent.

## Representation of the results by a differential equation

$$dx/dt = k_1'(\text{IO}_3)/V \times 2.303 \dots\dots\dots (\text{p. 469})$$

$$k_1' = k_1 + 7.4 \times 10^9 \times (\text{I}_2) \times (\text{I}) \times (\text{H})^2 \times 1/V^4 \cdot (\text{D, p. 470})$$

$$k_1 = \frac{K \times 1^{1.9} \times (\text{H})^2}{2.303 \times V^4} \dots\dots\dots (\text{B, p. 466})$$

$$\text{Let } R = 7.4 \times 10^9 \times 2.303 \dots\dots\dots (\text{E})$$

Then the general differential equation may be written

$$\begin{aligned} \frac{dx}{dt} = K \left( \frac{\text{IO}_3 - x}{V} \right) \left( \frac{\text{I} - y}{V} \right)^{1.9} \left( \frac{\text{H}}{V} \right)^2 \\ + R \left( \frac{\text{IO}_3 - x}{V} \right) \left( \frac{\text{I} - y}{V} \right) \left( \frac{\text{I}_2}{V} \right) \left( \frac{\text{H}}{V} \right)^2 \dots\dots\dots (\text{F}) \end{aligned}$$

or more simply

$$\frac{dx}{dt} = (\text{IO}_3) \cdot (\text{I}) \cdot (\text{H})^2 \left\{ \frac{K(\text{I})^{0.9} + R(\text{I}_2)}{V^6} \right\} \dots\dots\dots (\text{G})$$

where

$$K = 2.54 \times 10^{10} \dots\dots\dots (\text{p. 467})$$

$$R = 1.70 \times 10^{10} \dots\dots\dots (\text{E})$$

TABLE 19

$\text{IO}_3$ , 0.000025; Iod, 40 cc; ( $\text{I}_2$ , 0.00183;  $\text{I}$ , 0.002053);  
HAc, 0.0058; NaAc, 0.0015;  $\text{H}$ , 0.000007

$t$	$Th$	$k_1' \times 10^3$
2	11.85	41.3
4	10.04	38.6
6	8.75	36.0
		Av. 38.6

TABLE 20

$\text{IO}_3$ , 0.000025; Iod, 20 cc; ( $\text{I}_2$ , 0.000915;  $\text{I}$ , 0.0010265);  
 $\text{I}$ , 0.000885; HAc, 0.0058; NaAc, 0.0015;  $\text{H}$ , 0.000007

$t$	$Th$	$k_1' \times 10^3$
2	12.60	27.9
4	11.24	26.4
6	9.72	28.1
8	8.60	27.7
		Av. 27.6

TABLE 21

$\text{IO}_3$ , 0.000025; Iod, 10 cc; ( $\text{I}_2$ , 0.000457;  $\text{I}$ , 0.0005133);  
 $\text{I}$ , 0.001328;  $\text{HAc}$ , 0.0058;  $\text{NaAc}$ , 0.0015;  $\text{H}$ , 0.000007

$t$	$T_h$	$k_1' \times 10^3$
2	12.97	21.7
4	11.66	23.4
6	10.20	24.6
8	9.05	24.9
		Av. 23.6

TABLE 22

$\text{IO}_3$ , 0.000025; Iod, 20 cc; ( $\text{I}_2$ , 0.000915;  $\text{I}$ , 0.0010265);  
 $\text{I}$ , 0.000885;  $\text{HAc}$ , 0.0117;  $\text{NaAc}$ , 0.0015;  $\text{H}$ , 0.000014

$t$	$T_h$	$k_1' \times 10^3$
1	11.09	111.3
1.5	9.35	123.6
2	7.90	129.3
		Av. 121.4

TABLE 23

$\text{IO}_3$ , 0.000050; Iod, 20 cc; ( $\text{I}_2$ , 0.000915;  $\text{I}$ , 0.0010265);  
 $\text{I}$ , 0.000885;  $\text{HAc}$ , 0.0058;  $\text{NaAc}$ , 0.0015;  $\text{H}$ , 0.000007

$t$	$T_h$	$k_1' \times 10^3$
1	26.58	31.3
2	24.51	32.8
3	23.94	(24.7)
4	22.20	27.7
		Av. 29.1

TABLE 24

$\text{IO}_3$ , 0.000025; Iod, 20 cc; ( $\text{I}_2$ , 0.000915;  $\text{I}$ , 0.0010265);  
 $\text{I}$ , 0.002655;  $\text{HAc}$ , 0.0058;  $\text{NaAc}$ , 0.0015;  $\text{H}$ , 0.000007

$t$	$T_h$	$k_1' \times 10^3$
1	12.99	73.8
1.5	10.70	(84.5)
2	10.00	78.1
3	8.17	81.5
		Av. 79.5

TABLE 25

$\text{IO}_3$ , 0.000025; Iod, 20 cc; ( $\text{I}_2$ , 0.000915;  $\text{I}$ , 0.0010265);  
 $\text{I}$ , 0.000885;  $\text{HAc}$ , 0.0058;  $\text{NaAc}$ , 0.0030;  $\text{H}$ , 0.0000035

$t$	$T_h$	$k_1' \times 10^3$
8	12.56	7.1
16	10.88	7.4
		Av. 7.3

TABLE 26

$\text{IO}_3$ , 0.000025; Iod, 10 cc; ( $\text{I}_2$ , 0.000457;  $\text{I}$ , 0.0005133);  
 $\text{I}$ , 0.0030975;  $\text{HAc}$ , 0.0058;  $\text{NaAc}$ , 0.0015;  $\text{H}$ , 0.000007

$t$	$T_h$	$k_1' \times 10^3$
1	12.24	68.5
2	10.09	76.2
3	8.62	73.5
4	7.51	70.2
		Av. 72.1

TABLE 27

$\text{IO}_3$ , 0.000025; Iod, 40 cc; ( $\text{I}_2$ , 0.00183;  $\text{I}$ , 0.002053);  
 $\text{I}$ , 0.00177;  $\text{HAc}$ , 0.0058;  $\text{NaAc}$ , 0.0015;  $\text{H}$ , 0.000007

$t$	$T_h$	$k_1' \times 10^3$
2	9.16	97.2



**SERIES IV. SOLUTIONS OF HYDRIODIC AND IODIC ACIDS**

Having determined the rates in solutions in which the components hydrion, iodion, and iodation, could each be controlled separately, it remained to carry out a few measurements with the acids themselves.

The results of these experiments are given in Tables 28 to 34, where the symbols used have the significance explained on page 458. The concentrations are given on the assumption that hydriodic and iodic acids are completely dissociated into their ions. In order to keep the rate within measurable limits only small quantities of each reagent could be used; the experimental errors in this series are therefore much larger than in the previous tables; but nevertheless the constants are very fair.

Before performing the experiments with the pure acids, the measurements of Series I to III were connected with those of the following series, by several determinations in solutions containing (i) acetic acid, sodium acetate, potassium iodate, hydriodic acid, and (ii) acetic acid, sodium acetate, potassium iodide, iodic acid, respectively. The results were in good agreement with the requirements of equation (A) page 466, and demonstrated the absence of catalyzers in the hydriodic and iodic acid solutions.

In Tables 28 to 31 the hydriodic acid was present in excess; in Tables 32 to 34 the iodic acid. The values of  $K$  (page 466) for all these experiments are collected in Table 35; with the exception of  $K$  for Table 33, they show fair agreement. The laws which have been discovered in the systematic experiments of the previous series thus hold also for solutions containing hydriodic and iodic acids only. The average value of  $K$  however (0.84) is much lower than that found with acetic acid solutions (2.54).

A small part of this difference may be ascribed to the assumption of total dissociation of the acids made in the calculation. Experiments in which sodium chloride was added to the acid solution (Table 36), without effect on the rate, show that the difference cannot be ascribed to acceleration by the sodium

ions introduced with the sodium acetate in the previous series.

If it be assumed that the rate is strictly proportional to the square of the concentration of the hydrogen-ion, there remains only the hypothesis that the calculation of the dissociation of acetic acid is faulty. If in Table 17  $H$  be set, not 0.000007 but 0.000012, the agreement is good; this corresponds to a value 0.00003 for the dissociation constant of acetic acid, however, which is entirely out of the question (see page 459). This is not the first time that the calculation of dissociation from conductivity measurements has given unsatisfactory results.

TABLE 28

$IO_3$ , 0.000005;  $I$ , 0.000564;  $H$ , 0.000569; Vol, 0.31 liter

$t$	$As$	$k_1 \times 10^3$
2	0.74	65.0
4	1.28	64.4
5	1.44	61.0
7	1.70	56.0

Av. 61.6

TABLE 29

$IO_3$ , 0.000010;  $I$ , 0.000564;  $H$ , 0.000574; Vol, 0.31 liter

$t$	$As$	$k_1 \times 10^3$
2	1.51	67.3
3	2.06	65.5
4	2.33	57.5

Av. 63.4

TABLE 30

$IO_3$ , 0.000005;  $I$ , 0.001128;  $H$ , 0.001133; Vol, 0.31 liter

$t$	$As$	$k_1 \times 10^3$
0.25	1.66	(1568.7)
0.5	2.30	1216.4
1.0	2.58	1010.0

Av. 1113.2

TABLE 31

IO<sub>3</sub>, 0.000005 ; I, 0.000564 ; H, 0.000569 ; Vol, 0.39 liter

$t$	$As$	$k_1 \times 10^3$
4	0.81	36.1
8	1.37	33.0
		Av. 34.6

TABLE 32

IO<sub>3</sub>, 0.0000488 ; I, 0.0000566 ; H, 0.0001054 ; Vol, 0.1 liter

$t$	$As$	$k_2$
4	0.45	540
8	0.84	578
		Av. 559

TABLE 33

IO<sub>3</sub>, 0.0000976 ; I, 0.0000556 ; H, 0.0001542 ; Vol, 0.1 liter

$t$	$As$	$k_2$
2	1.02	2984
3	1.35	2956
4	1.60	2899
		Av. 2946

TABLE 34

IO<sub>3</sub>, 0.0000488 ; I, 0.0001132 ; H, 0.0001620 ; Vol, 0.1 liter

$t$	$As$	$k_2$
2	1.60	1100
3	2.28	1114
4	2.56	1064
		Av. 1093

TABLE 35

No.	$V$	$IO_3 \times 10^3$	$I \times 10^3$	$H \times 10^3$
28	0.31	5.0	564.0	569.0
29	0.31	10.0	564.0	574.0
30	0.31	5.0	1128.0	1133.0
31	0.39	5.0	564.0	569.0
32	0.10	48.8	56.6	105.4
33	0.10	97.6	56.6	154.2
34	0.10	48.8	113.2	162.0

No.	$k_1 \times 10^3$	$k_2$	$K \times 10^{-10}$
28	61.6	—	0.62
29	63.4	—	0.64
30	1113.2	—	0.82
31	34.6	—	0.70
32	—	559.0	1.00
33	—	2946.0	1.25
34	—	1093.0	0.83

Av. 0.84

TABLE 36

5 cc F/10 NaCl;  $IO_3$ , 0.000005; I, 0.000564; H, 0.000569;  
Vol, 0.31 liter

$t$	$As$	$k_1 \times 10^3$
2	0.75	66.0
4	1.22	60.4
5	1.43	60.2

Av. 62.2

TABLE 37

10 cc F/10 NaCl;  $IO_3$ , 0.000005; I, 0.000564; H, 0.000569;  
Vol, 0.31 liter

$t$	$As$	$k_1 \times 10^3$
2	0.70	61.0
4	1.21	60.0
5	1.45	61.4

Av. 60.8

**SERIES V. HYDRIODIC AND IODIC ACIDS, IODINE (TRI-IODION)  
PRESENT IN EXCESS**

Tables 39 to 41 give the results of measurements with the solutions of hydriodic and iodic acids to which an excess of iodine was added in the form of hydrogen tri-iodide ( $\text{HI}_3$ ). As the results of this series are in full agreement with those of Series III, I shall merely add the following table (38) to show that the effect of tri-iodion on the rate between the pure acids is governed by the same laws as its effect when in presence of neutral salts (sodium acetate and potassium salts in Series III). The meanings of the symbols are the same as in the tables of Series III. In order to facilitate comparison of Series V with Series IV, I have recalculated the corresponding values of  $k_1$  in the former series for the same concentration of iodion as in Tables 39 to 41 (assuming that the rate is proportional to the square of the concentration of the iodion). These numbers are entered under  $k_1$ .

TABLE 38

No.	$IO_3 \times 10^6$	$I \times 10^6$	$H \times 10^6$	$I_3 \times 10^6$
39	5	356	569	208
40	10	356	574	208
41	5	712	1133	416

No.	$k_1' \times 10^3$	$k_1 \times 10^3$	$(k_1' - k_1) \times 10^3$	S
39	67.0	25.0	42.0	1.7
40	59.5	25.3	34.2	1.4
41	882.0	443.0	439.0	1.2

Av. 1.4

The constancy of the quotient,

$$S = \frac{(k_1' - k_1) \times 10^{-12}}{(I_3) \times (H)^2 \times (I)} \dots\dots\dots (H)$$

shows that the rate, in the presence of an excess of iodine, is proportional to the square of the concentration of the hydrion, to the first power of that of the iodion and to the first power of that of the tri-iodion.

The results of Series IV and V may thus be represented by the differential equations (F) and (G), of page 471, which served for Series I-III; the numerical values of  $K$  and  $R$  however, are different.

$$K = 0.84 \times 10^{10} \text{ (instead of } 2.54 \times 10^{10} \text{, page 471)}$$

$$R = 0.32 \times 10^{10} \text{ (instead of } 1.70 \times 10^{10} \text{, page 471)}$$

TABLE 39

$\text{IO}_3$ , 0.00005;  $\text{I}$ , 0.00005;  $\text{I}_2$ , 0.000208;  $\text{H}$ , 0.000569; Vol, 0.31

$t$	$Th$	$k_1' \times 10^3$
1	2.37	81.7
2	2.15	62.0
2.5	1.90	71.0
5	1.33	66.5
7	1.20	54.0

Av. 67.0

TABLE 40

$\text{IO}_3$ , 0.000010;  $\text{I}$ , 0.000356;  $\text{I}_2$ , 0.000208;  $\text{H}$ , 0.000574; Vol, 0.31

$t$	$Th$	$k_1' \times 10^3$
2	4.35	59.5
3	4.00	(52.0)

Av. 59.5

TABLE 41

$\text{IO}_3$ , 0.000005;  $\text{I}$ , 0.000712;  $\text{I}_2$ , 0.000416;  $\text{H}$ , 0.001133; Vol, 0.31

$t$	$Th$	$k_1' \times 10^3$
0.5	1.13	807
0.75	0.59	914
1.0	0.34	925

Av. 882

## V. TEMPERATURE COEFFICIENT

The measurements of Table 1 (at 0° C) were repeated at a temperature of 37° C, and one measurement was made at 14° C. The results are given in Table 42.

TABLE 42  
 $\text{IO}_3$ , 0.000025;  $\text{I}$ , 0.00177;  $\text{HAc}$ , 0.00585;  $\text{NaAc}$ , 0.0015;  
 $\text{H}$ , 0.000007

Temp.	$t$	$As$	$k_1 \times 10^3$	$K \times 10^{-10}$
37° C.	2	2.68	44.0	—
"	4	4.63	43.0	—
"	6	6.18	41.0	—
			Av. 42.6	5.90
14° C.	4	3.23	28.0	3.90
0° C.	—	—	18.3	2.54

The rate rises almost *linearly* with the temperature, a rise from zero to 10° C multiplying the rate by about 1.4. This is one of the lowest temperature coefficients on record.<sup>1</sup>

## VI. EFFECT OF LIGHT AND OF CATALYZERS

Experiments with solutions of hydriodic and iodic acids in which, by means of a concave mirror, direct sunlight was concentrated on the reacting mixture in the beaker, gave the same results as those carried out in the diffuse light of the laboratory.

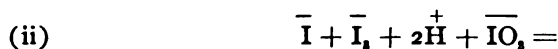
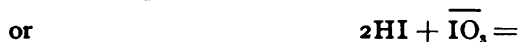
By means of a few measurements it was found that potassium bichromate does not affect the rate and that ferrous sulphate accelerates only moderately.

## VII. MOLECULAR INTERPRETATION OF THE RESULTS

The form of the differential equation found above suggests the simultaneous occurrence of two reactions in solutions con-

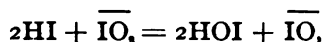
<sup>1</sup> See DeLury. Jour. Phys. Chem. 7, 251 (1903).

taining iodide, iodate, acid and free iodine, corresponding to the chemical equations



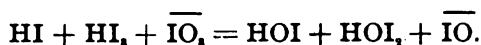
in which the indices of the differential equations serve as coefficients.

The right-hand member of equation (i) may be filled in conjecturally thus,



giving HOI and its ion  $\bar{OI}$  as the oxidation product of HI and reduction product of  $\bar{IO}_3$  respectively. This assumption is in accordance with Roebuck's work on the reaction between arsenious acid and hydrogen iodide,<sup>1</sup> and with the current views on oxidation in organic chemistry, where the series of oxidation products of methyl alcohol, for instance, are regarded as derived from  $CH_4$  by successive introduction of O between H and the electronegative element.

It is more difficult to invent a right-hand member for equation (ii); the following, however, might serve if it be supposed that the substance  $I_2OH$  (invented *ad hoc*) straightway decomposes into  $I_2$  and  $IOH$ .



My thanks are due to Prof. W. Lash Miller, at whose suggestion this research was undertaken, and under whose supervision it has been carried out.

*The University of Toronto,  
June, 1904.*

<sup>1</sup> Jour. Phys. Chem. 6, 365 (1902).



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# ON THE DEPOSITION OF ZINC FROM ZINC CHLORIDE DISSOLVED IN ACETONE

BY HARRISON EASTMAN PATTEN

## Introduction

The electrolysis of zinc chloride in acetone solution possesses interest from several standpoints. First as to the physical state and purity of the zinc deposited; second, concerning the current density and voltage requisite to deposit the zinc; and finally as to the use of this solution for chlorination at the anode, especially when the anode itself is corroded.

## Experimental

Fused zinc chloride was dissolved in acetone<sup>1</sup> to saturation and subjected to electrolysis between polished platinum electrodes 0.7 cm apart and 3 square centimeters in area.<sup>2</sup> Table I gives the current and current density corresponding to various pressures<sup>3</sup> in Plate 1. Current density is plotted as a function of the voltage, using amperes per square centimeter as abscissas and volts as ordinates. The points lie on a very regular curve; especially considering the enlarged scale to which they are plotted.

The residual current shows a current E. M. F. curve which approaches closely a straight line. That it is not the true CR line of the solution is seen by comparison with the CR line of the upper part of the curve after passing the bend. This higher CR line gives a specific resistance of 33.42 ohms for the solution corresponding to a specific conductivity of  $2.99 \times 10^{-2}$  at 20.5°, the temperature of the experiment.

<sup>1</sup> The acetone was dried over fused calcium chloride and distilled.

<sup>2</sup> A cut and description of the cell used may be found on page 318, Vol. III, Trans. Am. Electrochemical Soc., 1903.

<sup>3</sup> For the method used see a former paper, "Decomposition Curves of Lithium Chloride and the Electrodeposition of Lithium," Jour. Phys. Chem., March, 1904.

TABLE I.  
Zinc Chloride in Acetone  
Platinum Electrodes  
Temperature 20.5° C

Volts	Amperes	Amperes Per sq. cm.
0.30	0.000(?)	—
0.40	0.0001	0.00003 +
0.50	0.0008	0.00026
0.60	0.001	0.00033
0.70	0.001	0.00033
0.80	0.0014	0.00046
0.90	0.0014	0.00046
1.00	0.0017	0.00057
1.10	0.0019	0.00063
1.20	0.0019	0.00063
1.30	0.0020	0.00067
1.40	0.0022	0.00074
1.50	0.0025	0.00084
1.60	0.0026	0.00087
1.70	0.0029	0.00097
1.80	0.0029	0.00097
1.90	0.0032	0.0010
2.00	0.0035	0.0011
2.10	0.0039	0.0012
2.20	0.0046	0.0015
2.30	0.006	0.002
2.40	0.0075	0.0025
2.50	0.0085	0.0028
2.70	0.010	0.0033
2.70	0.0114	0.0038
2.80	0.013	0.0040
2.90	0.0145	0.0048
3.00	0.0159	0.0053
3.00	0.0182	0.0060
3.50	0.0264	0.0088
4.00	0.0337	0.0112
4.50	0.0419	0.0139
5.00	0.051	0.017
5.50	0.060	0.020
6.00	0.068	0.0226
7.00	0.086	0.028
8.00	0.103	0.034
9.00	0.120	0.040
10.00	0.140	0.046
12.00	0.180	0.060

By producing the CR line to the axis of volts a decomposition point of 1.90 volts is obtained. Wiedeburg's method of drawing the straight portions of the curve out to their intersection gives 2.14 volts. And the E. M. F. corresponding to the current density at the bend of the curve is near 2 volts, the value given in the abstract of this article.<sup>1</sup>

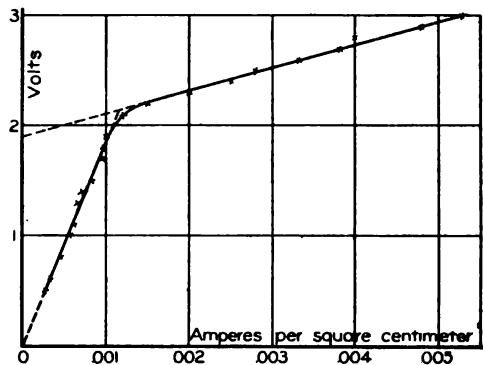


Plate I.  
ZnCl<sub>2</sub> in acetone  
Platinum electrodes  
 $t = 20.5^{\circ} \text{C.}$

During the first stage<sup>2</sup> of electrolysis a discharge potential of 1.27 volts was obtained from a current density of 0.0006 ampere per square centimeter. In this experiment no gas bubbles appeared at either electrode. However in later experiments gas came off upon the cathode, though by no means copiously. Chloroform, chloracetone or other alkyl chlorides were formed at the anode,<sup>3 4 5</sup> and a compact smooth coating of zinc was deposited upon the cathode. Zinc may be deposited steadily with a current density as low as 2.00 amperes per square foot, though the current efficiency is low. With a current density of 40 amperes per square foot, the zinc trees out from the edges of the

<sup>1</sup> *Electrochemical Industry*, August, 1903.

<sup>2</sup> See the treatment of primary electrolysis of the solute given in a former paper, "Decomposition Curves of Lithium Chloride," etc., l. c.

<sup>3</sup> E. Schering. *D. R. P.*, 29, 771, May 6, 1884.

<sup>4</sup> Howe Abbott. *Jour. Phys. Chem.* 7, 84 (1903).

<sup>5</sup> J. E. Teeple. *Jour. Am. Chem. Soc.* 26, 170 (1904).

cathode in long streamers. Use of a rotating cathode would tend to obviate this difficulty. Later experiments have shown that the zinc becomes spongy when the depth of coating exceeds about one millimeter, and before this pits appear. Analysis gave between 0.9 and 1.0 percent of carbon in the deposit.

On standing over night a zinc deposit redissolved in the solution from which it was obtained. From the above facts it appears that the deposition of zinc from acetone solution is not well adapted to procure chemically pure zinc or to give a thick coat for chemical purposes, and the preparation of zinc free from carbon is still before us.

With the best so-called c. p. zinc electrodes as anode and cathode a current E. M. F. curve was determined in this same acetone solution of zinc chloride at 20° C, as shown in Table II and Plate 2.

TABLE II.  
Zinc Chloride in Acetone  
Zinc Electrodes  
Temperature 20° C

Volts	Amperes	Amperes Per sq. cm.
0.037	0.000197	0.0000558
0.043	0.000257	0.0000754
0.048	0.000352	0.000103
0.065	0.000435	0.000128
0.074	0.000526	0.000154
0.091	0.000609	0.000178
0.099	0.000701	0.000203
0.109	0.000791	0.000232
0.125	0.000875	0.000256
0.138	0.000962	0.000282
0.154	0.00105	0.000307
0.178	0.00122	0.000357
0.212	0.00139	0.000407
0.260	0.00174	0.000510
0.443	0.00306	0.000898
0.502	0.00350	0.000103

For low voltage there is a slight indication of polarization,

but comparison with the points for higher voltages shows that these deviations are due to experimental error. The zinc anode was evenly corroded. Using a fresh saturated solution of zinc chloride in acetone a weighed zinc anode was corroded with an average current density of 0.0124 amperes per square centimeter until 4.6451 grams of zinc had dissolved away. The solution was then filtered from the spongy zinc and distilled, using a tower. The acetone was recovered intact, boiling at  $54.7^{\circ}$  to  $55.0^{\circ}$  C under a pressure of 738.8 mm.

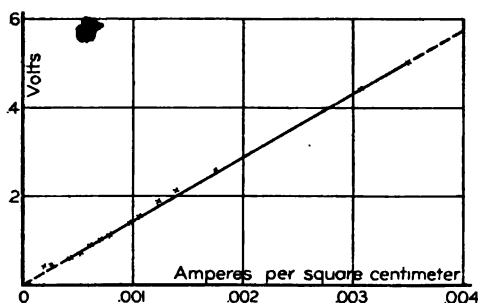


Plate II.  
ZnCl<sub>2</sub> in acetone  
Zinc electrodes  
 $t = 20^{\circ}$  C

This experiment is of general bearing as quantitative evidence that a solvent subject to attack by an acid radicle may be used for continuous refinement where the anode is readily attacked. This confirms the lack of polarization shown in Plate 2. All of the liberated chlorine is fixed by the zinc. A number of other metals similarly electrolyzed in acetone solution of their chlorides show no polarization.

This work was done in the laboratories of physical chemistry and of applied electrochemistry, and the author takes pleasure in expressing his appreciation of the courtesy extended to him by both.

*University of Wisconsin,  
June 22, 1904.*

## ON THE STABILITY OF THE EQUILIBRIUM OF MULTIVARIANT SYSTEMS

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BY PAUL SAUREL

The following properties of an  $n$ -component bivariant system are well-known :

At a given temperature and under a given pressure  $n$ -phases can coexist in equilibrium. At the given temperature and under the given pressure the state of equilibrium of the system is determinate, that is to say, the masses of the phases and their concentrations are determinate. There exist, however, exceptional states of the system such that, without changing the temperature or the pressure, the system can be subjected to a reversible change during which the entropy and the volume of the system and the masses of the phases change, while the concentrations of the phases and the total thermodynamic potential of the system remain constant. The state of equilibrium becomes determinate if, in addition to the masses of the components, the volume or the entropy of the system be given. These exceptional states of bivariant systems are called indifferent points.

By removing one of the  $n$ -phases of the bivariant system we can form  $n$  different trivariant systems. Each of these systems can be in equilibrium at a series of temperatures and under a series of pressures. The temperature and the pressure can be chosen independently, but then the state of equilibrium of the trivariant system is completely determined.

If, starting at the temperature and under the pressure of the indifferent point of the bivariant system, we keep the pressure of any one of the derived trivariant systems constant but vary its temperature, it will be found that the equilibrium of the trivariant system will be stable at temperatures higher than that of the indifferent point, and unstable at temperatures lower than that of the indifferent point, or else that the equilibrium will be unstable at the higher and stable at the lower temperatures.

In like manner, if we keep the temperature equal to that of the indifferent point and allow the pressure to vary, it will be found that the equilibrium of any one of the derived trivariant systems will be stable for pressures on one side of the pressure of the indifferent point and unstable for pressures on the other side of that pressure.

The following two theorems enable us to distinguish the stable from the unstable states of equilibrium of the trivariant systems.

I. Consider the bivariant system in equilibrium at an indifferent point. Without changing the temperature or the pressure of the system, let us subject it to a reversible change which increases its entropy. During this change, the mass of each phase will, in general, change; the masses of certain of the phases increase while the masses of the others decrease. If the mass of the  $i$ -th phase increases, then the  $i$ -th trivariant system, that is to say, the trivariant system in which the  $i$ -th phase is lacking, cannot exist in stable equilibrium under the given pressure at temperatures higher than that of the indifferent point. If, on the contrary, the mass of the  $i$ -th phase diminishes, then the  $i$ -th trivariant system cannot exist at temperatures lower than that of the indifferent point.

II. Consider the bivariant system in equilibrium at an indifferent point. Without changing the temperature or the pressure of the system, let us subject it to a reversible change which diminishes its volume. During this change, the mass of each phase will, in general, change; the masses of certain of the phases increase while the masses of the others decrease. If the mass of the  $i$ -th phase increases, then the  $i$ -th trivariant system cannot exist in stable equilibrium at the given temperature under pressures greater than that of the indifferent point. If, on the contrary, the mass of the  $i$ -th phase diminishes, then the  $i$ -th trivariant system cannot exist under pressures lower than that of the indifferent point.

To establish these theorems it is sufficient to repeat verbatim the demonstration by which we have established the correspond-



ing theorems for the bivariant systems which can be derived from a given univariant system.<sup>1</sup> We consider the  $i$ -th trivariant system in equilibrium at an indifferent point of the original bivariant system. Without changing the temperature or the pressure we can cause the  $i$ -th phase to appear. This necessitates a certain change in the entropy and a corresponding change in the volume of the system. If we denote the total thermodynamic potential, the entropy and the volume of the system in the first state of equilibrium by  $\Phi_1$ ,  $H_1$ ,  $V_1$ , and in the second state of equilibrium by  $\Phi_2$ ,  $H_2$ ,  $V_2$ , the various conditions and equations given in the previous note become at once applicable.

For the sake of clearness we have, in the statement of the two theorems, spoken of a bivariant system and the derived trivariant systems, but it is obvious that the same theorems hold for the different systems that can be derived from a multivariant system at an indifferent point by suppressing one of its phases.

*New York, April 24, 1904.*

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<sup>1</sup> Jour. Phys. Chem. 8, 436 (1904).

## ON INDIFFERENT POINTS

BY PAUL SAUREL

A bivariant or multivariant system is said to be at an indifferent point when the system admits of a continuous series of states of equilibrium during which the temperature, the pressure and the concentrations remain constant while the masses of the phases change. The indifferent points of a bivariate or multivariate system form a series analogous to the series of states of equilibrium of a univariate system, that is to say, at a given temperature, the pressure and the concentrations of the corresponding indifferent point are determinate. We may accordingly construct in the temperature-pressure plane a curve, each point of which will represent the temperature and the pressure of an indifferent point. The slope of this curve at any point is given by the equation,

$$\frac{d\Pi}{dT} = \frac{\delta H}{\delta V},$$

which is in all respects similar to Clapeyron's equation for univariate systems. In this equation  $T$  represents the temperature of the indifferent point,  $\Pi$  its pressure, and  $\delta H$  and  $\delta V$  the changes in the entropy and the volume of the system due to a reversible change at the temperature and under the pressure of the indifferent point.

An indifferent point of a bivariate or multivariate system possesses, moreover, the following properties:

The temperature of the indifferent point is, in general, a maximum or a minimum of the temperatures at which the system can exist in equilibrium under the given pressure.

The pressure of the indifferent point is, in general, a maximum or a minimum of the pressures under which the system can exist in equilibrium at the given temperature.

It follows immediately from these theorems that the indifferent curve divides the plane into two regions such that at temperatures and under pressures corresponding to points on one

side of the curve the bivalent or multivalent system can exist in equilibrium, while at temperatures and under pressures corresponding to points on the other side of the curve the system cannot exist in equilibrium.

The properties of indifferent points which we have just recalled, lead at once to the following theorem :

Consider a bivalent or multivalent system at an indifferent point under a pressure  $\Pi$  and at a temperature  $T$ . If a reversible change at the temperature  $T$  and under the pressure  $\Pi$  involves changes  $\delta H$  and  $\delta V$  of entropy and of volume which have the same sign, then either the temperature  $T$  is a maximum of the temperatures at which the system can exist under the pressure  $\Pi$  and the pressure  $\Pi$  is a minimum of the pressures under which the system can exist at the temperature  $T$ , or, vice versa, the temperature  $T$  is a minimum and the pressure  $\Pi$  a maximum. If, on the contrary, the reversible change at the temperature and under the pressure of the indifferent point involves changes of entropy and of volume which differ in sign, then  $T$  is a maximum temperature and  $\Pi$  a maximum pressure, or  $T$  is a minimum temperature and  $\Pi$  a minimum pressure.

To establish this theorem, we observe that if  $\delta H$  and  $\delta V$  have the same sign the indifferent curve slopes upward from left to right. Since the indifferent curve divides the plane into two regions, in one of which the bivalent or multivalent system can exist in equilibrium while in the other it cannot, it follows at once from the diagram that a maximum temperature is associated with a minimum pressure or, vice versa, a minimum temperature with a maximum pressure. If, on the contrary,  $\delta H$  and  $\delta V$  have opposite signs, the indifferent curve slopes downward from left to right. It follows at once that a maximum temperature is associated with a maximum pressure and a minimum temperature with a minimum pressure.

For the indifferent points of bivalent binary and ternary systems and of trivalent ternary systems this theorem is due to Gibbs.<sup>1</sup>

*New York, April 23, 1904.*

<sup>1</sup> Trans. Conn. Acad. 3, 183-187 (1876).

## THE SOLUBILITY OF CALCIUM SULPHATE IN SOLUTIONS OF NITRATES<sup>1</sup>

BY ATHERTON SEIDELL AND JOSEPH G. SMITH

The solubility of gypsum in aqueous salt solutions has been studied by a number of investigators and has from time to time been given attention in this laboratory.<sup>2</sup> A careful examination of the literature upon solubility determinations of mixtures of salts, shows that of all substances the solubility of calcium sulphate has been investigated in probably a larger number of different salt solutions than that of any other compound.<sup>3</sup> It, therefore, appears to offer the best opportunity for a comparative study of the increasing or diminishing solubility effects produced by more or less concentrated aqueous solutions of different salts. A difficulty, however, presents itself at once, in that the data are to a considerable extent only qualitative, and in the earlier papers, where quantitative results are given, these are usually in such form as to make a strict comparison with more modern work almost impossible. The work described in this paper was undertaken for the purpose of extending the systematic observations which have so far been made in this laboratory and elsewhere upon the solubility of calcium sulphate in aqueous salt solutions.

The solubility of calcium sulphate in ammonium nitrate solutions has been observed by Fassbender,<sup>4</sup> but his experiments were more or less qualitative only. Droeze<sup>5</sup> determined the solubility of gypsum in saturated solutions and in some cases other concentrations of the nitrates of ammonium, sodium, potassium and magnesium, but his figures are rather indefinite,

<sup>1</sup> Published by permission of the Secretary of Agriculture.

<sup>2</sup> Jour. Phys. Chem. 5, 643 (1901); Ibid. 7, 571 (1903); Ibid. 8, 335 (1904).

<sup>3</sup> Bibliography of Solubilities, by Atherton Seidell, soon to be published.

<sup>4</sup> Ber. chem. Ges. Berlin, 9, 1360 (1876).

<sup>5</sup> Ibid. 10, 330 (1877).

since one cannot determine from the description the precise concentrations employed, and an accurate comparison of his results with those observed later cannot be made. Making the comparisons, however, as best one may, quite large discrepancies are found, and it is evident that his results as well as those already mentioned are mainly useful in showing the directions of the solubility changes in the systems studied. Cohn<sup>1</sup> gives determinations of the solubility of calcium sulphate in ammonium nitrate and in several other ammonium salts. The results of the calcium sulphate determinations are presented in terms of grams dissolved per 100 grams of solution, while the concentrations of the ammonium salt employed are stated in percentages of a standard solution, contained in 100 grams of water. By a tedious and indirect method it has been possible to recalculate the results to grams of salts contained in 100 cc of solution, and in this form to compare them with similar determinations made by another investigator. The results of this comparison for one of the salts employed, viz.: ammonium chloride, which was studied by Ditte,<sup>2</sup> shows a difference which is too great to be accounted for by ordinary analytical error. It appears that Cohn's results are subject to the criticisms applied above to other investigations.

From the preceding it is evident that satisfactory determinations of the solubility of calcium sulphate in solutions of nitrates have so far not been made. In order, therefore, to extend the observations to this class of compounds, the following experiments were undertaken:

#### **Experimental Part**

Saturated solutions of the nitrates of sodium, potassium, calcium and magnesium were prepared, and after being filtered and slightly diluted, the grams of salt per liter of solution were determined by evaporating to dryness and weighing in the case of the sodium nitrate and potassium nitrate, and by determining the calcium and magnesium gravimetrically and calculating to

<sup>1</sup> Jour. prakt. Chem. (2) 34, 43 (1887).

<sup>2</sup> Comptes rendus, 126, 674 (1898); Ann. Chim. Phys. (7) 14, 294 (1898).

the anhydrous salt in the case of the calcium nitrate and magnesium nitrate solutions. The concentrated standard solutions thus prepared were diluted and the required amount to give 200 cc portions of the solutions containing the amounts per liter of dissolved salts indicated in the tables. To the 200 cc portions of the solutions of various concentrations was added an excess of finely powdered calcium sulphate (calcium sulphate — Merck, precip. — pure) and the mixtures, contained in bottles of about 250 cc capacity, kept at room temperature with frequent shaking for several days and then rotated in a constant temperature bath at 25° C for at least 24 hours and then allowed to settle previous to withdrawing portions for analysis from the clear supernatant solutions. Two 50 cc portions were withdrawn in every case. One of these was transferred to a weighing bottle and after being weighed was transferred to a beaker and used for the determination of the sulphates by the usual method of precipitation and weighing as barium sulphate. The other 50 cc portion was used for the determination of the calcium which was precipitated as oxalate and weighed in the usual manner as oxide.

TABLE I.  
Calcium Sulphate in Solutions of Sodium Nitrate

Weight of 1000 cc. of solution	Grams $\text{NaNO}_3$ per liter	Grams $\text{CaSO}_4$ per liter
998.1	0	2.084
1016.3	25	4.252
1034.0	50	5.500
1068.4	100	7.100
1133.6	200	8.790
1191.6	300	9.282
1363.9	600	7.886
1390.4	655	7.238

In Table I are given the results obtained with solutions of varying concentrations in sodium nitrate. All results are given in grams per liter of solution, although the weight of the solution is also given, making it possible to compute the solubility on the basis of mass of solvent instead of volume of solution.

The results show that the solubility of the calcium sulphate increases to a marked degree in concentrations of sodium nitrate up to 300 grams per liter, but beyond this concentration the amount dissolved becomes less as the concentration of the nitrate increases.

In the second table the results obtained in solutions of potassium nitrate are given.

TABLE II.  
Calcium Sulphate in Solutions of Potassium Nitrate

Weight of 1000 cc. of solution	Grams $\text{KNO}_3$ per liter	Grams $\text{CaSO}_4$ per liter
998.1	0.0	2.084
1008.1	12.5	3.284
1015.4	25.0	4.080
1032.1	50.0	5.255
1062.5	100.0	6.855
1092.4	150.0	7.907
1122.4	200.0	8.688
1153.9	260.0	{ 6.278 <sup>1</sup> 12.112 <sup>2</sup>

In these solutions both the calcium and the sulphate were determined as in the preceding case. Up to a concentration of 200 grams of potassium nitrate per liter, the amount of calcium sulphate in solution steadily increases, and the sulphate determinations agree with the calcium determinations, that is, the amount of calcium sulphate is the same whether calculated from the sulphate or calcium determinations. Beyond this concentration the sulphate and calcium determinations no longer agree, and differ very widely in fact, as is indicated in the table. This phenomenon was noticed whenever a potassium salt solution is used, but the concentration where this disagreement occurs varies with the different salts. This is probably due to the formation of a new solid phase, the double salt of calcium and potassium sulphates,  $\text{CaK}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ , or syngenite, and beyond this

<sup>1</sup> Calculated from  $\text{SO}_4$  determination.

<sup>2</sup> Calculated from Ca determination.

point the solubility of calcium sulphate as such is no longer observed.

In the third table the results obtained in solutions of magnesium nitrate are given. The determinations of the relatively small amounts of calcium in the presence of the larger amounts of magnesium were not made on account of the difficulty of obtaining a satisfactory separation of the calcium. The sulphate determinations were, however, made in duplicate, and the results in the last column are calculated from these determinations.

TABLE III.  
Calcium Sulphate in Solutions of Magnesium Nitrate

Weight of 1000 cc. of solution	Grams $\text{Mg}(\text{NO}_3)_2$ per liter	Grams $\text{CaSO}_4$ per liter
998.1	0	2.084
1020.5	25	5.772
1039.8	50	7.884
1078.6	100	9.920
1149.8	200	13.340
1219.0	300	14.000
1282.1	400	14.683
1355.3	514	15.040

The solubility, as is seen, steadily increases to such an extent that magnesium nitrate solutions have by far the greatest solvent effect on calcium sulphate yet observed. In an almost saturated solution of magnesium nitrate, it is more than seven times as great as in pure water.

The results also seem to indicate the absence of any maximum value. This is the only case so far observed where solutions of a salt containing neither a calcium nor a sulphate ion have failed to show a maximum value of the calcium sulphate in solution in the higher concentrations of the salts.

The results obtained with solutions of calcium nitrate are given in the fourth table. Here again the calcium determinations were omitted, and the results given in the last column are based wholly on the sulphate determinations which were made in duplicate.



The results show that the calcium nitrate decreases the solubility of the sulphate to a marked degree, with increasing concentration of the nitrate.

TABLE IV.  
Calcium Sulphate in Solutions of Calcium Nitrate

Weight of 1000 cc. of solution	Grams $\text{Ca}(\text{NO}_3)_2$ per liter	Grams $\text{CaSO}_4$ per liter
998.1	0	2.084
1013.8	25	1.238
1031.7	50	1.196
1067.3	100	1.134
1136.9	200	0.929
1203.5	300	0.759
1265.6	400	0.569
1328.1	500	0.403
1352.0	544	0.346

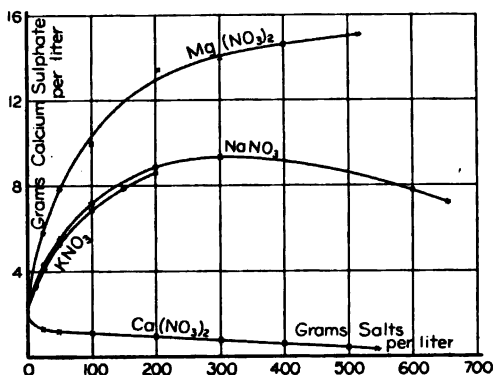


Fig. 1

The above results with the four nitrate solutions are perhaps better seen from the accompanying graphic representation. The curves show very markedly the varying effects of the different salt solutions on the solubility of the calcium sulphate. Magnesium nitrate increases the solubility greatly. Sodium nitrate and potassium nitrate have about the same increasing effect; the sodium nitrate shows the customary maximum values in the higher concentrations of salts containing no com-

mon ion ; the potassium nitrate is not plotted beyond the point where syngenite separated. The calcium nitrate depressed the solubility. In general, when no common ion is present the solubility is increased, while a common ion decreases the solubility. The decrease in the higher concentration of the sodium nitrate remains, however, unexplained by this general statement and is probably connected with the formation of molecular complexes with the solvent itself in these higher concentrations.

It may be of interest in this connection to state that a comparison of the solubility of calcium sulphate in the solutions of the nitrates here employed with the results obtained with the corresponding chlorides shows that in general a greater increase of solubility is noticed in the case of the nitrates.

In conclusion the authors wish to thank Dr. F. K. Cameron for his kindly interest and advice.

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## THE DISSOCIATION POINTS OF SOME CHLORIDES

BY PETER FIREMAN AND E. G. PORTNER

When potassium or ammonium iodide is brought closely to the fumes given off by antimony pentachloride, a reddish-brown precipitate forms on the surface of the iodide. If the pulverized iodide is spread over a strip of white paper or a piece of porcelain the reaction presents the beautiful phenomenon of a cloud passing rapidly over the surface prepared for it and leaving a charred appearance in its track.

We had frequent occasion to observe this phenomenon in a study of the action of the iodides mentioned on antimony pentachloride, and the idea gradually impressed itself upon us that we were confronted with a rather interesting chemical reaction, that the reddish-brown superficial layer — obviously free iodine — might be separated by free chlorine, due to the dissociation of antimony pentachloride at ordinary temperature. It appeared of interest to look more closely into this matter.

First of all we confirmed, by the potassium iodide and starch test, that the reddish-brown precipitate was really free iodine. A like precipitate, spreading also like a cloud, is formed when free chlorine is allowed to pass over powdered potassium iodide. In both cases the thin reddish-brown layer volatilizes in a short time.

On the other hand, we found that when powdered potassium iodide is dropped into antimonious chloride the reaction, whatever it may be, proceeds at ordinary temperature only to a very slight extent, and that if the bodies are heated in a sealed tube at not too high temperatures ( $120^{\circ}$ – $140^{\circ}$ ) antimony pentiodide is copiously formed.<sup>1</sup>

Now antimony pentiodide which has scarcely been prepared in a state approaching purity, is known to be a most unstable body, rapidly decomposing with the liberation of iodine. It

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<sup>1</sup> In a future communication this subject will be fully treated.

might be supposed that such is the origin of the reddish-brown precipitate on potassium iodide in the presence of fumes of antimonious chloride.

Again, the iodine could be conceived as resulting through the action of moisture, the latter starting a series of reactions (formation of hydrochloric acid, setting free of hydriodic acid, and breaking up of the latter) terminating in the separation of iodine.

In either of these cases, however, the instantaneous spreading of the reddish-brown precipitate on potassium iodide, with "the cloud effect" would remain unaccounted for. Moreover, if the iodine were the product of the decomposition of antimonious iodide, appreciable traces of antimonious iodide should be left on the volatilization of the iodine, which is not the case.

The most plausible conclusion from the above observations seems to be that the iodine is liberated by free chlorine, due to antimony pentachloride, or, at least, its vapor, being dissociated at ordinary temperatures. If this conclusion is correct, then such compounds as stannic chloride or titanium tetrachloride, which fume in the air like antimony pentachloride, but which are not known to dissociate, should not give the "cloud effect" on potassium iodide (free iodine), while such as phosphorous pentachloride should behave like antimonious chloride.

To begin with stannic chloride. The fumes of the latter acting on powdered potassium iodide turn it first yellow, then orange-yellow, and lastly, orange-red. Obviously, some stannic iodide is formed. On moist potassium iodide starch paper the fumes produce no effect on short exposure; only after a few minutes a slight blue coloration, which may be considered as resulting from the decomposition of hydriodic acid, formed either by the action of hydrochloric acid on potassium iodide, or by that of moisture on stannic iodide, or by both.

Titanium tetrachloride acts less readily on potassium iodide, with or without starch solution. Even copious fumes of the chloride do not seem to affect either of the reagents named. Only when some drops of the titanium compound are poured

over pulverized potassium iodide, some titanium tetriodide is formed, which first appears as a light brown precipitate turning soon darker, then reddish-brown; after some time the potassium iodide is left with a yellow tinge. On moist potassium iodide starch paper liquid titanium tetrachloride gives a blue coloration, along with a light-brown precipitate.

On the other hand, phosphorus pentachloride acts on dry potassium iodide as well as on a solution of the latter and starch, exactly as antimonie chloride does, provided it is heated. In other words, if antimony pentachloride is dissociated at ordinary temperatures, phosphorus pentachloride is so only at higher temperatures. The experiments are suitably carried out in a test-tube and either of the reagents is held over its mouth.

Like the pentachlorides of antimony and phosphorus, *be-* have also ferric, cupric, and chromic chloride. In all these cases heat has to be applied, but by far not such high temperatures are required as one would be inclined to suppose. Any way, the fact of the dissociation of the chlorides just mentioned can most readily be demonstrated by a very simple test-tube experiment.

It occurred to us of interest, and as feasible, to ascertain the lowest temperatures at which the chlorides under consideration show distinctly the fact of their dissociation; to ascertain — let us use the term — their “dissociation points.”

We attempted to determine the dissociation points by bringing the substances into test-tubes in sufficient quantity to bury the bulb of the thermometer in them, and then heating in a bath of paraffin or fusible metal. In these experiments, however, moist potassium iodide starch paper was used to detect the first traces of chlorine.

Phosphorus pentachloride sublimes at about  $100^{\circ}$ , condensing a short distance above the level of the bath, and shows the first signs of chlorine at  $157^{\circ}$ – $158^{\circ}$ . The decomposition seems to set in energetically, judging from the rapidity with which the entire surface of the test paper becomes blue. After a few minutes, no more free chlorine can be detected at the mouth of the test-tube, the temperature, however, remaining constantly at

about  $158^{\circ}$  for a long time: On forcing the temperature higher, chlorine again escapes from the tube. Apparently, phosphorus trichloride, one of the products of the dissociation, on distilling and condensing on the ring of sublimed phosphorus pentachloride, absorbs, after a while, the chlorine passing upward.

The same results were obtained with phosphorus pentachloride from different lots, and in short and long test-tubes alike.

Ferric chloride, anhydrous, begins to dissociate at  $122^{\circ}$ – $123^{\circ}$ . To obtain a constant dissociation point the ferric chloride must be well dried, otherwise the decomposition begins at considerably higher temperatures. Also, in this case, the experiments were carried out in both short and long test-tubes with the same result. Victor Meyer<sup>1</sup> and Grünbaum could discover ferrous chloride as a product of the decomposition of ferric chloride only after the latter had been heated above  $448^{\circ}$ .

Cupric chloride, anhydrous, shows the first signs of dissociation at  $344^{\circ}$ .

Chromic chloride, anhydrous, begins to dissociate at  $355^{\circ}$ .

We think that by the cumulative evidence in the foregoing, we have established beyond a doubt that in the experiments described above with the higher chlorides of antimony, phosphorus, iron, copper, and chromium, we were confronted with the same reaction, that of dissociation.

In further support of this view, we want to emphasize the following points:

In the cases of cupric and chromic chloride, everybody must at once admit that the reaction in question cannot be anything else but a pure dissociation, it being quite impossible for these chlorides, as well as the lower ones to which they are reduced, to reach the mouth of the test-tube at the temperature indicated above.

And the apparent reaction is in every way the same, also, in the cases of the chlorides of antimony, phosphorus, and iron;

<sup>1</sup> Ber. chem. Ges. Berlin, 21, 687 (1888).

this uniformity is remarkable and suggestive of a common nature.

Lastly, the constant temperature at which the chlorine reaction sets in, in each case, is weighty evidence in favor of the view propounded. It need not be overlooked in this connection that the constancy of what we call "the dissociation point" is the more significant in view of the fact that it is independent of the length of the test-tube in which the reaction is carried out; this constancy of temperature would be out of the question if a volatilization of the chlorides and their coming in contact with the potassium iodide were necessary to initiate the reaction.

We believe to have indicated a simple general test for the dissociation of chlorides; a test well suited for demonstration in the lecture. We further believe to have determined the "dissociation points" of a number of chlorides, being the first data for establishing a new constant.

We intend to pursue the subject further.

*Alexandria, Va.*

## NEW BOOKS

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Wilhelm Ostwald. By P. Walden. 16 × 24 cm; pp. 120. Leipzig: Wilhelm Engelmann, 1904. Price: paper, 4 marks. — Ostwald was born in Riga in 1853. He took the first degree at Dorpat in 1875 and the doctor's degree in 1878. From 1875–1880 he was assistant in the physical laboratory; in 1880 he was appointed assistant in the chemical laboratory; and in 1881 he was called to Riga as professor of chemistry at the polytechnic institute. In the six years at Riga, Ostwald increased the attendance in the laboratory from eighty-one to two hundred and ten; he published a series of papers in the *Journal für praktische Chemie*; he wrote the first edition of the *Lehrbuch*; and he started the *Zeitschrift für physikalische Chemie*. It is little wonder that Ostwald's friends were able to convince the powers that be that Ostwald was the man for the vacant chair of physical chemistry in Leipzig. As a matter of fact, this was not accomplished easily, and it was only owing to the determined stand taken by a few men that Ostwald was called to Leipzig in 1887. Another bit of inside history, which does not appear in Walden's sketch, is that Ostwald's first plan was to make the *Journal für praktische Chemie* the organ for physical chemistry. The editor could not see any advantage in this and it was then that Ostwald started the *Zeitschrift für physikalische Chemie*.

The first year at Leipzig must have been a discouraging one. The second semester there was only one man studying physical chemistry. This state of things did not last. In the third semester there were eight advanced students and thirteen in the fourth. The time soon came when people worked in the halls and the cellar. In 1898 the new laboratory was opened and even this is now overcrowded.

The change in the scientific status of Ostwald has been a remarkable one. In 1890 the electrolytic dissociation was fighting for recognition. Nernst's paper on the voltaic cell had been published but had attracted very little attention. The general feeling of chemists toward Ostwald was that he was an able man who was wasting his talents. Some went so far as to deny his claim to being a chemist. Any idea held by Ostwald was *per se* an object of suspicion. To-day the opposition to the electrolytic dissociation theory comes from those who believe that it has outlived its usefulness. Ostwald is recognized as one of the leading chemists of the world, and any opinion of his is promptly accepted as dogma by a large and enthusiastic following.

Ostwald is essentially a leader of men. The theory of solutions was furnished by van 't Hoff; the theory of electrolytic dissociation by Arrhenius; the theory of the voltaic cell by Nernst. Not one of these three important generalizations is due to Ostwald; but he has taken all three, developed them and brought them to recognition and acceptance as no one else could have done. Nernst's theory of the voltaic cell lay dead until Ostwald took it up. Everything about the theory of electrolytic dissociation except the formulation is due to Ostwald. No one believes that Arrhenius could have overcome the



opposition of the chemists. It was Ostwald who brought the theory of osmotic pressure to the front. The work of Beckmann, done in Ostwald's laboratory, made the testing of the theory a simple matter, while Ostwald himself lost no opportunity to impress people with the importance of the theory.

It is as a leader rather than as a pioneer that we must consider Ostwald. The pioneer discovers the new land; but his discovery will come to nothing if the people do not follow him and take possession of the country. The pioneer is independent of the world. He must have a clear insight and courage. The leader must not be too far ahead of his followers. He must be working toward the same goal as they and he must be able to help them forward. He is handicapped by the fact that he cannot move faster than the army can follow him; but this is more than balanced by the fact that every advance is held.

To some it has seemed that Ostwald's point of view has not changed in the last ten years as much as it should have done. This may or may not be true. It is true, however, that the chemical world has been brought up to Ostwald's position by Ostwald; and there are a few who hope and believe that Ostwald's Faraday lecture is the signal for a new and a rapid advance. It may well be so. For seventeen years the bulk of the work in physical chemistry has been devoted to dilute solutions, largely as a result of Ostwald's personal influence. So great is his influence that he could change this inside of a twelve-month. Ostwald exerts a tremendous power in the chemical world to-day. If he will devote himself to chemistry instead of to philosophy and will throw his influence in favor of progress, there is before him another era of triumphant achievement, compared to which the results of the past decade will appear trivial. If he does not do this, the world will still move on, though not so rapidly as might have been the case.

In this biographical sketch by Walden we see how Ostwald has developed and how the promise of the boy has been fulfilled in the man. One of the most interesting things in the book is the letter written by C. Schmidt in 1881, urging Ostwald's appointment at Riga. It shows how accurately a clear-sighted man could judge Ostwald even then. This and much else is to be found in the little pamphlet, which will be read with much interest by all chemists.

*Wilder D. Bancroft*

**Grundriss der physikalischen Chemie.** By J. Traube. 16 × 25 cm; pp. viii + 360. Stuttgart: Ferdinand Enke, 1904. Price: paper, 9 marks. — The object of the author has been to write a non-mathematical treatise in which each part of the subject should be given its due amount of space. The first seventy pages deal with the laws of the conservation of mass and of energy, with the second law of thermodynamics, and with the atomic theory. The next one hundred and fifty pages are devoted to chemical statics, while chemical energetics are treated in the remainder of the book. Under chemical energetics we find the mass law relations for equilibrium and reaction velocity, thermochemistry, the phase rule, electrochemistry, photochemistry and radiochemistry.

The author believes in the existence of atoms but not of ions. This means that the distribution of space is very different from that in most textbooks on physical chemistry. Thus reaction velocity is disposed of in less than

thirteen pages. A great deal is said about the properties of liquid and vapor. While the book is not a great one, it is interesting reading, though the author has laid more stress on physics than on chemistry. In one place, page 73, there is a curious inversion of ideas. The author starts with the hypothesis of Avogadro and deduces from it that the gas constant  $R$  must be the same for all gases.

Wilder D. Bancroft

*Jahrbuch der Elektrochemie. Berichte über die Fortschritte des Jahres 1902. Herausgegeben von Heinrich Danneel. IX. Jahrgang. 16 × 24 cm; pp. ix + 750. Halle: Wilhelm Knapp, 1904. Price: paper, 24 marks.* — This volume is more interesting than the preceding ones. The delay in publication is of course unfortunate because many of the points taken up are ancient history by this time. The editor states in the preface that the next volume will appear more promptly.

Among the interesting features of 1902 were: the work of Richards on the voltameter; the general discussion of valence and affinity; the physiological applications of electrochemistry; Kohlrausch's work on water; the elastic atoms of Richards; the papers on oxidation cells; and the work of Kahlenberg on instantaneous reactions. The editor does not look upon Kahlenberg's experiments as proving that reactions can take place when no ions are present. "For there are ion concentrations, which cannot be detected by the most sensitive methods, but which are sufficient to cause a rapid reaction if the undissociated molecules furnish new ions sufficiently fast, i. e., if the rate of dissociation is as infinitely great as the ion concentration is infinitely small." When one remembers that Goldschmidt has shown that the undissociated substances are the active masses in certain reactions, one wonders why there should be this frantic desire to make all reactions ion reactions. It has not proved itself a useful working hypothesis and therefore, by definition, it is valueless for the present.

There are two excellent chapters on catalysis, one under pure chemistry and the other under applied chemistry. One may question whether the work of Sabatier and Senderens can properly be classed under electrochemistry as yet; but the experiments are interesting in themselves. There is an amusing section on the so-called application of physical chemistry to the analysis of mineral springs, and an interesting one on electrical phenomena in gases.

Under applied electrochemistry, the most interesting things are the Edison cell, the Betts process, the Mauran improvements in the Castner soda process, and the use of the electric furnace for iron and steel. The account of the Niagara plant for making nitric acid from the air is one of the things which was more important in 1902 than in 1904.

Wilder D. Bancroft

*Electricity and Matter. By J. J. Thomson. 13 × 20 cm; pp. 162. New York: Charles Scribner's Sons, 1904.* — The great art underlying this fascinating book is the presentation, in a way accessible to everybody, of results which have been arrived at by the most refined laboratory method and the most profound thought. One is astounded to find in so involved a subject that the equations and the mechanism needed for description are so very simple. The author is filled with ideas to communicate, and the style and language used

become almost conversational. If it takes art to conceal art, it requires the very highest genius spontaneously to detect the elements of order and simplicity in an apparently chaotic play of nature. Even those who have followed the Cambridge school, will find the book throughout bristling with novelty and suggestion, and adequately to review it would require more space than the little volume (in large type) contains. Suffice it, then, to say that the first lecture deals interpretatively with lines of force, Faraday tubes as they are called; and the properties ascribed to such tubes by Faraday and Maxwell are further particularized and developed. The second chapter is an electromagnetic interpretation of mass. The third evolves a definitely specialized mechanism for light and Röntgen ray vibrations. The fourth summarizes the knowledge gained of the mass and the charge of the corpuscle. The next lecture, on the constitution of the atom, is the longest and most interesting in this interesting book, and it is pleasant to find Mayer's experiments with floating magnets once more brought into prominence, here in explanation of the periodic law. The series closes with a lecture on radioactivity, which is only less interesting because more familiar. Some glaring misprints mar the text, as for instance,  $\gamma$  for  $r$  on page 57,  $v$  for  $V$  on p. 68, "our" for "one" on p. 74,  $A_s$  for  $A_x$  on p. 136. Briefly, however, this is a book which every reader must review for himself; and the Mrs. Hepsa Ely Silliman Foundation may well be proud of the success of its inaugural venture.

C. Barus

**La Théorie de Maxwell et les Oscillations Hertiennes; la Télégraphie sans Fil.** By H. Poincaré. *Scientia*, No. 23).  $13 \times 20$  cm; pp. vi + 32. Paris: C. Naud, 1904. Price: 2 francs. — This little book seems to be a second edition of No. 1 of the same series, with the last section added. The whole collection is admirably selected and edited, and aims to give a more or less authoritative account of remarkable advances in physics and mathematics, at the earliest practicable opportunity. The books are "popular" for a physicist, and the general plan seems to have been copied by the series called *Wissenschaft* reviewed elsewhere. It is surprising that a man like the author, who is among the most active of the abstruse mathematical thinkers of the day, should find time and inclination to make these summaries of experimental work; but M. Poincaré is none the less an ideal compiler, with a knack not only to diffuse the charm of his transparent style into every page, but to enliven it with his trenchant and often inexorable criticism. Take this, for instance: "La structure compliquée qu'il (Maxwell) attribuait à l'éther rendait son système bizarre et rébarbatif; on aurait cru lire la description d'une usine avec des engrenages, des billes transmettant le mouvement et fléchis sous l'effort, des régulateurs à boules et des courrois." But he adds: "... Quel que soit le gout des Anglais pour ce genre de conceptions ... sa pensée ... a été ainsi conduite aux plus grand découvertes."

Relatively little space is devoted to Maxwell's theory, the bulk of the book being a succinct analysis of our knowledge of electric oscillations and their applications in practice. All is clear except the description of apparatus (like that of Fizeau and Gounelle or of Blondlot) by letters; this no doubt saves the author the trouble of supplying a figure, but it soon ends with the reader in a blur of vexation, particularly when certain technical words are missed. In all

other respects the book is so full of well digested experimental information, and the tone throughout so appreciative of experimental methods that one would never suspect the mathematician.

In his short chapter on wireless telegraphy, Poincaré scoffs at any obscure rôle played either by the antennæ or by the soil. He refers all observations to the facilitated diffraction of very long electric waves.

C. Barus

**Die Chemie der Zuckerarten.** By Edmund O. von Lippmann. 14 X 23 cm. *Erster Halbband*: xxxviii + 1034 pp. *Zweiter Halbband*: 1035-2003 pp. Braunschweig: Friedrich Vieweg und Sohn, 1904. Price: paper, 30; bound, 34 marks. — The first volume deals with the monosaccharides, the chief sub-heads being: dioses, trioses, tetroses and methyl derivatives; pentoses and methyl pentoses; hexoses and methyl hexoses; heptoses, octoses, nonoses and methyl derivatives; cycloses. The second volume deals with the disaccharides, the trisaccharides and the tetrasaccharides. The whole forms a monumental work, certainly beyond the power of any one man to read intelligently, even though it was written by a single man. For the immediate present the physical chemist will probably be most interested in the part of the second volume which treats of cane-sugar. Under physical properties the author discusses: crystals (forms, index of refraction, triboluminescence, pyro-electricity, dielectric constant, conductivity for heat and electricity, compression, melting-point); specific gravity (heat expansion of solutions, cubical expansion, reduction of specific gravities, contraction); boiling-points; solubility and nature of solution; viscosity; transpiration, internal friction; diffusion; osmose and osmotic pressure; dialysis; surface tension and capillarity; vapor pressure and rise of boiling-point; lowering of freezing-point; electrical conductivity, effect of salts on conductivity, dielectric constant; solubility of salts and other substances in sugar solutions, formation of molasses; solubility of gases in sugar solutions; heat properties; optical properties. In addition the author discusses the behavior of sugar on heating and on dry distillation; the effect of reagents, including under this head the rate of inversion; the fermentation of sugar and action of enzymes; compounds; detection and determination.

There are many points which need further study. Wulff's conclusions, p. 1093, as to the existence of amorphous sugar in solution are obviously unsound and the matter should be taken up again from the standpoint that amorphous sugar is a liquid. The solubility of cane-sugar in invert sugar, p. 1098, is one of those things which we dismiss with the remark, "change of solvent". The formation of molasses, p. 1161, is another matter which would well repay study by the physical chemist. We are quite in the dark as to the action of sodium chloride, etc., p. 1186, on the specific rotation of sugar. The chapter on the syntheses of the sugars, successful and unsuccessful, will be of interest to all physical chemists.

The book is admirable in conception and in execution. The more of such monographs we can have, the better it will be for chemistry.

Wilder D. Bancroft

**Die Kathodenstrahlen.** By G. C. Schmidt. (*Die Wissenschaft. Sammlung naturwissenschaftlicher und mathematischer Monographien. Heft 2.*)

14 × 22 cm; pp. vi + 120. Braunschweig: Friedrich Vieweg und Sohn, 1904. Price: paper, 3 marks; bound, 3.60 marks. — The author, who has made noteworthy contributions to our knowledge of radioactivity, here gives a popular but accurate account of the present state of advance of the subject. The bibliography is very full. The pamphlet is well systematized, and the treatment clear-cut and readable. After brief introductory chapters, relating among other things to methods of producing the cathode rays, potential gradients, the effect of electrostatic and of magnetic fields, energy and velocity, the Zeeman effect (following the beautiful method of Lorentz),  $e$  and  $m$ , apparent mass, reflection, absorption, etc., are each taken up in order and thoroughly discussed. Anybody interested in this rapidly developing subject will find the book full of valuable information. Good figures are given throughout. C. Barus

**L'Industrie de la Soude.** By L. Guillet. (*Encyclopédie des Aide-Mémoire.*) 11 × 19 cm; pp. 178. Paris: Gauthier-Villars; Masson et Cie. Price: paper, 2.5; boards, 3 francs. — The subjects treated in the book are: sodium chloride, sodium carbonate, sodium hydroxide, sodium, sodium peroxide. Like all the other volumes of the series, this one gives a general view of the subject without making any special claim to accuracy. The Acker process, for instance, is not mentioned, and the Rhodin process receives more space than does the Castner process. On the other hand, the account of the development of the Solvay process is interesting reading. Wilder D. Bancroft

**Ready Reference Tables.** By Carl Hering. Vol. I.: *Conversion Factors.* 10 × 17 cm; pp. xviii + 196. New York: John Wiley and Sons, 1904. Price: bound, \$2.50. — The title page tells us that this volume contains "conversion factors of every unit or measure in use, including those of length, surface, volume, capacity, weight, weight and length, pressure, weight and volume, weight of water, energy, heat, power, force, inertia, moments, velocity, acceleration, angles, grades, time, electricity, magnetism, electrochemistry, light, temperature, money, money and length, money and weight, numerous compound units, useful functions and numbers, etc., etc., with their accurate and approximate values, their logarithms, relations, digit conversion tables, explanations of calculations, etc., etc., based on the accurate legal standard values of the United States." The book is very convenient in size and arrangement. While it does not fall within the avowed scope, the reviewer feels that it would have been well, in a book published in 1904, to have called attention to the fact that the legal volt is certainly not the true volt. Wilder D. Bancroft

## REVIEWS

*The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry*

### General

**Emanation of radium, its properties and changes.** *W. Ramsay. Comptes rendus*, 138, 1388 (1904). — The emanation from radium bromide behaves like an ordinary gas, follows the gas law, and has a density of about 80 with reference to hydrogen as one. As it is probably a monatomic gas like the members of the argon group, it has a molecular weight of 160. The author considers it as a new, though fleeting element, and calls it exradio. Assuming that one atomic weight of radium yields one atomic weight of exradio, the rate of change is such that one atomic weight of radium would have disappeared at the end of eleven hundred years. The lines in the spectrum of exradio which are intense and lasting have the wave-lengths 5805, 5725, 5595, 5105, 4985. Exradio disappears gradually, helium being formed. The reverse reaction has not yet been effected nor has exradio been carried back into radium. *W. D. B.*

**Atomic weight of nitrogen.** *P. A. Guye and S. Bogdan. Comptes rendus*, 138, 1494 (1904). — The authors have burned iron in  $N_2O$ . The atomic weight for nitrogen comes out 14.007. While this value is not final, it is believed to be much nearer the truth than the one ordinarily accepted. The authors feel quite certain that the true value does not exceed 14.01. *W. D. B.*

**Europium.** *G. Urbain and H. Lacombe. Comptes rendus*, 138, 627 (1904). — The atomic weight of europium was determined by dehydrating the hydrated sulphate and also by conversion of the hydrated or anhydrous sulphate into the oxide. The final value is 151.79. *W. D. B.*

**The atomic weight of samarium.** *G. Urbain and H. Lacombe. Comptes rendus*, 138, 1166 (1904). — The samarium was free from europium and gadolinium. The atomic weight was found to be 150.34. *W. D. B.*

**On the distribution of the chemical elements in the earth and its possible relation to their atomic weights.** *K. De Launay. Comptes rendus*, 138, 712 (1904). — The author believes that the geological facts warrant the assumption that the elements arranged themselves at first at distances from the center of the earth varying inversely as their atomic weight. The general distribution in groups counting from the outside was :

1. Hydrogen (1).
2. Nitrogen (14); oxygen (16).
3. Sodium (23); magnesium (24); aluminum (27); silicon (28).
4. Phosphorus (31); sulphur (32); chlorine (35).

5. Titanium (40); vanadium (51); chromium (52); manganese (55); iron (56); nickel and cobalt (59).

6. Copper (64).

7. Zinc (65); silver (108); antimony (120); tungsten (184); gold (197); mercury (200); lead (207); bismuth (208); radium (225); uranium (239).

W. D. B.

**Elementary demonstration of the phase rule.** *C. Raveau. Comptes rendus, 138, 621 (1904).* — The demonstration "is based on the experimental characteristics of reversible equilibrium in heterogeneous systems."

W. D. B.

**Simple demonstrations of the phase rule.** *A. Ponsot. Comptes rendus, 138, 690 (1904).* — Three demonstrations of the phase rule.

W. D. B.

**The conception of independent components, II.** *R. Wegscheider. Zeit. phys. Chem. 45, 496 (1903).* — The author continues to struggle with the question whether the system ammonium chloride is a one-component system or not. The question was settled years ago but reappears whenever some one "discovers" the phase rule. If the composition of each phase is constant and is the same as the composition of all the other phases, it is quite immaterial whether one treats the system as a one-component system or as a two-component system with one limiting condition. Since both ammonia and hydrochloric acid are volatile, and since the sublimation temperature is lower than the melting-point, ammonium chloride behaves at atmospheric pressure like a one-component system. If one works under conditions to give liquid ammonium chloride, we get the characteristics of a two-component system. This has been overlooked by the author.

W. D. B.

**The exceptions to the phase rule, especially with optically-active substances.** *A. Byk. Zeit. phys. Chem. 45, 465 (1903).* — The author discusses the apparent exceptions to the phase rule in the case of the two optically-active forms of sodium chlorate and then considers the possibility of  $n + 3$  phases. The author does not treat the subject as simply as it can be done.

The gist of the matter is this. With  $n + 2$  phases a system has no degrees of freedom. Any number of other phases can co-exist provided they satisfy the conditions for an invariant system and introduce no new ones. If we could find a substance which formed a eutectic with sulphur at  $96^\circ$  we should have five phases in equilibrium. Substances are known which form eutectic mixtures with sulphur above and below the inversion temperature for rhombic and monoclinic sulphur, and there is therefore no theoretical reason why one should not be found which would satisfy the conditions. On the other hand the probability of the eutectic temperature coinciding with the inversion point of sulphur to a hundredth of a degree is very small. In sodium chlorate we have a substance occurring in two solid phases which do not differ in regard to their pressure-temperature-concentration relations. This is therefore a case in which  $n + 3$  phases occur.

W. D. B.

**Comment on a paper by Mr. Byk.** *R. Wegscheider. Zeit. phys. Chem. 45, 697 (1903).* — The author objects to Byk's method of calculating the extreme improbability of  $n + 3$  phases occurring (preceding review).

W. D. B.

**Application of the phase rule to the precipitation of colloids.** *V. Henri and A. Mayer. Comptes rendus, 138, 757 (1904).* — The authors consider that a colloidal solution may be considered as a two-phase system in which the surface tension is an important factor. They also suggest the possibility of treating a colloidal solution as a one-phase system, ignoring the surface tension effect. This second way is purely formal and can hardly be considered as satisfactory. The authors announce that the phase rule is of great value in considering and classifying colloidal solutions. That is of course very satisfactory, but one would like a little more detail.  
W. D. B.

**Surface tension and gravity as factors of equilibrium.** *A. Ponsot. Comptes rendus, 138, 803 (1904).* — The author discusses surface tension and gravity in their bearing on the phase rule, but without deducing anything which was not already known.  
W. D. B.

**Calculation of heats of combustion of organic nitrogen compounds.** *P. Lemoult. Comptes rendus, 138, 900 (1904).* — The author develops a formula for the heats of combustion of organic compounds containing nitrogen.  
W. D. B.

**Apparatus for regulating vacuum pumps.** *J. Meunier. Comptes rendus, 138, 693 (1904).* — A device for closing the pump automatically whenever the pressure changes suddenly. This prevents water from being sucked back..  
W. D. B.

#### One-Component Systems

**The melting-point of gold.** *D. Berthelot. Comptes rendus, 138, 1153 (1904).* — In 1898 D. Berthelot gave  $1065.6^\circ$  as the melting-point of gold. In 1900 Holborn and Day found  $1064.3^\circ$ , while Jacquerod and Perrot obtained  $1067.4^\circ$  in 1904. The mean of these three determinations is  $1065.8^\circ$ , practically identical with the value of D. Berthelot.  
W. D. B.

**Some physical constants of the fluorides of phosphorus.** *H. Moissan. Comptes rendus, 138, 789 (1904).* — Phosphorus trifluoride melts at  $-160^\circ$  and boils at  $-95^\circ$ . The pentafluoride melts at  $-83^\circ$  and boils at  $-75^\circ$ , while the oxyfluoride,  $\text{POF}_3$ , melts at  $-68^\circ$  and boils at  $-40^\circ$ .  
W. D. B.

**New method for the exact determination of the molecular weights of the permanent gases.** *P. A. Guye. Comptes rendus, 138, 1213 (1904).* — The author writes the gas equation in the form

$$V_m(1+a)(1-b) = R + mT,$$

where  $V_m$  is the volume of one molecular weight at  $0^\circ$  under a pressure of one atmosphere and  $m$  is a constant having the value 0.08473. The calculations of the atomic weights of hydrogen and carbon from the gases oxygen, hydrogen, and carbon monoxide give values corresponding closely with the atomic weights found by chemical methods. This is not the case for nitrogen. The author states his belief that his atomic weight of 14.005 for nitrogen is nearer the truth than Stas's value of 14.04.  
W. D. B.



The more accurate gas equation. *J. B. Goebel. Zeit. phys. Chem.* 47, 471 (1904). — The author modifies the van der Waals equation, writing

$$p = \frac{RT}{v - b_0 - b_1 p} - \frac{a}{(v - a)^2}$$

For carbon dioxide, ethylene and nitrous oxide  $b_1$  is apparently zero, while it is about 0.000001 for nitrogen, oxygen and air. *W. D. B.*

New investigations on the density of fluorine. *H. Moissan. Comptes rendus*, 138, 728 (1904). — A new series of experiments on the density of fluorine give 1.298, 1.319, 1.313, 1.312, mean 1.31. The theoretical density is  $19.05 \times 0.06927 = 1.319$ . There is therefore no reason for assuming any dissociation of fluorine. *W. D. B.*

A new carbide of molybdenum, MoC. *H. Moissan and K. Hoffmann. Comptes rendus*, 138, 1558 (1904). — The carbide Mo<sub>3</sub>C had been prepared previously and the authors now describe the carbide MoC. It is prepared by heating molybdenum, carbon and aluminium in excess together in the electric furnace. The temperature is practically that at which aluminum boils. The carbide is attacked readily by nitric acid, only slightly by other acids. Cold water does not act upon it and neither does water vapor at 600°. The substance does not change when heated to a red heat in a current of hydrogen. The carbide forms prismatic crystals with a density of 8.4 at +20°. The hardness is between 7 and 8. *W. D. B.*

#### Two-Component Systems

Gypsum and anhydrite. *J. H. van't Hoff, E. F. Armstrong, W. Hinrichsen, F. Weigert, and G. Just. Zeit. phys. Chem.* 45, 257 (1903). — The slowness with which gypsum loses water makes a determination of the dissociation pressure very difficult. A sodium chloride solution increases the solubility and a dissociation pressure of 758.8 mm was found at 101.45°. At temperatures below 76° magnesium chloride was substituted for sodium chloride and the determinations were made in a tensimeter instead of by the boiling-point method. The quadruple point for gypsum, the half-hydrate, solution and vapor occurs at 107°, the pressure being 970 mm.

The change of gypsum into soluble anhydrite takes place at a lower temperature than the change into the half-hydrate. The temperature of the quadruple point was calculated at 93°; but this could not be checked satisfactorily owing to the formation of insoluble anhydrite. The quadruple point for gypsum, the insoluble anhydrite, solution and vapor occurs at 66° according to the calculations.

A study of the hydraulic plaster shows that when gypsum is first dehydrated at 190°, it retains the power of taking up water readily. This is gradually lost by longer heating or by raising the temperature. *W. D. B.*

The alloys of zinc and aluminum. *H. Pécheux. Comptes rendus*, 138, 1103 (1904). — The author believes that zinc and aluminum form nine compounds, Zn<sub>3</sub>Al, Zn<sub>2</sub>Al, ZnAl, AlAl<sub>2</sub>, ZnAl<sub>3</sub>, ZnAl<sub>4</sub>, ZnAl<sub>5</sub>, ZnAl<sub>10</sub>, ZnAl<sub>11</sub>. Unpublished experiments, made in the reviewer's laboratory, show that zinc and aluminum form two series of solid solutions and no compounds. One series

contains up to a few percent of aluminum, the other up to about fifty percent of zinc. *W. D. B.*

**The alloys of aluminum with magnesium, antimony and bismuth.** *H. Pêcheux. Comptes rendus*, 138, 1502, 1606 (1904). — By heating in a sealed tube Boudouard had prepared what he believed to be  $MgAl_4$ ,  $MgAl$  and  $MgAl_2$ . The author states that it is impossible in a crucible to obtain an alloy containing less than 65 percent aluminum which shall be stable in the air.

The author has prepared the alleged compounds  $SbAl_{30}$ ,  $SbAl_{35}$ ,  $SbAl_{38}$  and  $SbAl_{40}$ . As the author offers no proof that these substances are compounds, one is quite justified in doubting their existence. The bismuth-aluminum alloys are homogeneous only when they contain 70 percent of aluminum. The author does not state what phases occur. *W. D. B.*

**A property of the tin-aluminum alloys.** *H. Pêcheux. Comptes rendus*, 138, 1170 (1904). — When the mythical compounds,  $Sn_3Al$ ,  $Sn_2Al$ ,  $SnAl$ ,  $Sn_2Al_3$ , are filed and plunged into cold water, the water is decomposed with evolution of hydrogen and oxygen. A preliminary heating of the alloys without filing has no effect. Boiling water is decomposed by these aluminum-tin alloys even though they have not been filed. *W. D. B.*

**Cryoscopic studies on solutions in antimony sulphide.** *J. Guinchant and P. Chrétien. Comptes rendus*, 138, 1269 (1904). — Antimony sulphide,  $Sb_2S_3$ , melts at  $540^\circ$ . The freezing-point constant is 790 from experiments with lead sulphide and silver sulphide as solutes. This corresponds to 16.7 cal for the heat of fusion, while the direct determination gave 17.5. Antimony dissolved in antimony sulphide lowers the freezing-point to an amount corresponding to a molecular weight of 113 instead of 120. Of course it is impossible to determine whether the solute is Sb or  $Sb.Sb_2S_3$ . *W. D. B.*

**Solubility of silicon in zinc and lead.** *H. Moissan and F. Siemens. Comptes rendus*, 138, 657 (1904). — The solubility of silicon in lead is 0.0024 part per hundred at  $1250^\circ$  and 0.78 part at  $1550^\circ$ . The solubility in zinc is 0.06 part per hundred at  $600^\circ$  and 1.62 parts at  $850^\circ$ . *W. D. B.*

**Solubility of silicon in silver.** *H. Moissan and F. Siemens. Comptes rendus*, 138, 1299 (1904). — At  $970^\circ$  silicon dissolves 9.2 parts in 100 of silver. At  $1470^\circ$  the solubility is 41.5 parts. When the silicon crystallizes from the melt about four parts per hundred of silver is in a new form soluble in hydrofluoric acid. This new form of silicon is crystalline and has a density of about 2.4. *W. D. B.*

**Solubility and size of crystals.** *G. A. Hulett. Zeit. phys. Chem.* 47, 357 (1904). — The author attributes to Kohlrausch a disbelief in the change of solubility with the size of the crystals. He then brings forward facts to prove the existence of such a relation. *W. D. B.*

**Comment on a paper by Mr. Hulett.** *F. Kohlrausch. Zeit. phys. Chem.* 47, 625 (1904). — As the author does not hold the views attributed to him by Hulett (preceding review), he looks upon Hulett's paper as superfluous. *W. D. B.*

**The molecular weight of glycogen.** *Z. Gatin-Gruzewska. Comptes ren-*

*du*, 138, 1631 (1904). — Sabanejew found an apparent molecular weight for glycogen of 1620 by a freezing-point determination. It is now found that the addition of nearly four grams to 100 cc of water changes the freezing-point by not over 0.0001°. This corresponds to an apparent molecular weight of about 700,000, which is absurd. There seems to be no question but that glycogen is practically insoluble in water. *W. D. B.*

The mutual solubilities of nicotine in water. *C. S. Hudson. Zeit. phys. Chem.* 47, 113 (1904). — Nicotine and water give a closed field for two liquid layers and vapor. The lower consolute temperature is at 60° and the higher one at 210°. Above 90° the nicotine layer is the upper one, while the reverse holds below 90°. The author attributes the miscibility of nicotine and water at the lower temperatures to the formation of an unknown nicotine hydrate which has a solvent action on the two components. Such a case occurs with chloral and water. If this is the true explanation, nicotine and water should form two instable liquid layers when mixed at temperatures below 60°. This experiment was not tried. *W. D. B.*

Formation of silicon hydride by direct synthesis from the elements. *E. Vigouroux. Comptes rendus*, 138, 1168 (1904). — Attention is called to the fact that in 1901 the author described the formation of silicon hydride when silicon is heated in hydrogen. *W. D. B.*

Apparent volatilization of silicon in hydrogen. *A. Dufour. Comptes rendus*, 138, 1169 (1904). — In Geissler tubes containing arsine, the arsenic is precipitated by the discharge and sublimes from the hot portion of the tube to the colder portions. In tubes containing silicon hydride there is an apparent sublimation; but it is not a true one because the silicon gathers in the dark portion and not necessarily in the colder portion of the tube. *W. D. B.*

Isomorphous mixtures of lime and lithia. *P. Lebeau. Comptes rendus*, 138, 1602 (1904). — When calcium and lithium carbonates are heated together under diminished pressure, the lime formed takes up lithium oxide. This is apparently due to the formation of a solid solution. The author assumes the existence of isomorphous mixtures, but the crystalline forms of the two substances are against this. Lithium carbonate and calcium carbonate apparently form a compound, but the author was unable to analyze it. *W. D. B.*

Expressing the concentration of solutions. *H. J. Hamburger. Zeit. phys. Chem.* 47, 495 (1904). — The author calls attention to the difference between 1 g mol per liter water and per liter solution. He makes the inaccurate statement that Ostwald's molar concentration refers to a liter of water. When one is dealing with molecules plus ions the author suggests either molion or speaking of osmotic concentration. *W. D. B.*

On the density of aqueous salt solutions considered as an additive property of the ions, and on the existence of hydrated ions. *P. Vaillant. Comptes rendus*, 138, 1210 (1904). — The author concludes that there is no appreciable volume change when an electrolyte dissociates; that most ions are anhydrous; that the hydroxyl, fluoride, sulphide and carbonate anions are hydrated, the formulas being  $\text{OH}\cdot\text{H}_2\text{O}$ ,  $\text{F}\cdot\text{H}_2\text{O}$ ,  $\text{S}\cdot\text{H}_2\text{O}$  and  $\text{CO}_3\cdot\text{H}_2\text{O}$ . *W. D. B.*

**A theory of colloids and suspensions.** *J. Billitzer. Zeit. phys. Chem.* 45, 307 (1903).—Colloids are readily precipitated by electrolytes even when the solution is not at the iso-electric point. The author assumes that a colloidal solution contains suspended particles which are charged differently from the liquid, so that we may consider the particles as cation and the solvent as anion or vice versa, as the case may be. Coagulation occurs under the influence of a precipitating ion which acts as a condensation nucleus. When colloidal platinum charged with air is precipitated by potassium chloride, it carries down caustic potash, setting free hydrochloric acid. It proved impossible however to measure absolute potentials by determining the exact conditions under which neither acid nor alkali is set free. Gelatine decreases the rate of precipitation owing to increased viscosity. Alcohol and other non-electrolytes often change the rate of coagulation by changing the potential difference.

One consequence of the author's point of view is that no reaction can take place when a colloid is precipitated by the same ion which it forms. This was tested by experiments with silver nitrate and colloidal silver. *W. D. B.*

#### *Multi-Component Systems*

**Equilibrium between iron, ferroferric oxide, hydrogen and vapor.** *G. Preuner. Zeit. phys. Chem.* 47, 385 (1904).—The author has repeated and extended Deville's measurements on the equilibrium



Equilibrium was reached from both sides, but the equilibrium constant varied nearly ten percent. This was attributed to an error introduced by the solubility of hydrogen in water. The calculation of the heat of reaction from the displacement of the equilibrium with the temperature gave  $Q_{900} = 11900$  cal, while the value from the thermochemical data is 42890 cal. The only explanation offered by the author is that a 'surface layer' may be the cause of the discrepancy. *W. D. B.*

**Action of silicon on water at a temperature near 100°.** *H. Moissan and F. Siemens. Comptes rendus*, 138, 989 (1904).—Pure amorphous silicon, the crystallized silicon of Deville and that of Wöhler all appear to act on water at about 100°, setting free hydrogen and forming hydrated silicic acid. Further experiments in platinum with distilled water showed that this reaction takes place only in presence of alkali. *W. D. B.*

**Reduction of silica by hydrogen.** *A. Dufour. Comptes rendus*, 138, 1101 (1904).—At high temperatures there is a reversible reaction between silica, hydrogen, silicon hydride and water. This explains the apparent devitrification of quartz tubes when worked in the oxyhydrogen flame. *W. D. B.*

**Theoretical study of the dissociation of oxyhaemoglobin.** *V. Henri. Comptes rendus*, 138, 572 (1904).—Hüfner assumed that one of oxyhaemoglobin is formed from one of haemoglobin and one of oxygen. The author shows that a better equilibrium constant is obtained if we assume that oxyhaemoglobin is made from two of haemoglobin and one of oxygen. The author was unsuccessful in his attempt to apply the van't Hoff formula to the change of

the equilibrium constant with the temperature. Further experiments are to be made. W. D. B.

**Properties of sodium sulphate solutions.** *C. Marie and R. Marquis. Zeit. phys. Chem.* 45, 566 (1903). — Reviewed (8, 302) from *Comptes rendus*, 136, 684 (1903).

**The decomposition of mercurous chloride by alkali chloride solutions.** *J. Gewecke. Zeit. phys. Chem.* 45, 684 (1903). —

1. The decomposition of calomel by alkali chlorides depends on the temperature and concentration of the chloride solutions.
2. The decomposition of calomel has practically no disturbing effect on calomel electrodes with very dilute solutions ( $< 0.02N$ ) though even here it is desirable to keep the temperature low and the solution free from air.
3. The effect of the oxygen of the air is not negligible.
4. If mercury is to be determined quantitatively as mercurous chloride, only a slight excess of the precipitating chloride should be permitted and the temperature should be kept as low as possible. W. D. B.

**Addition to my paper on mercury halides.** *M. S. Sherrill. Zeit. phys. Chem.* 47, 103 (1904). — In the original paper (7, 545) it was assumed that mercuric chloride dissociated without formation of  $HgCl^+$ . This assumption is now dropped and the necessary corrections made. W. D. B.

**The hydrolysis of mercuric chloride.** *R. Luther. Zeit. phys. Chem.* 47, 107 (1904). — In Sherrill's calculations (preceding review) he has neglected the hydrolysis of mercuric chloride. Luther shows that such a hydrolysis occurs and discusses the consequences. It is interesting to note that one can make three different assumptions in regard to mercuric chloride solutions and each one leads to a formula which agrees 'satisfactorily' with the experimental data. W. D. B.

**Combination of sugar with some metallic salts.** *D. Gauthier. Comptes rendus*, 138, 638 (1904). — Sugar is shown to form compounds with sodium, potassium and lithium iodides; with ammonium, potassium, sodium and barium sulphocyanate. The double iodides have the general formula  $C_{12}H_{22}O_{11} \cdot RI \cdot 2H_2O$ . W. D. B.

**Vapor pressure in the system, benzene, carbon tetrachloride, and ethyl alcohol.** *F. A. H. Schreinemakers. Zeit. phys. Chem.* 47, 445; 48, 257 (1904). — Benzene and alcohol give a minimum boiling-point and so do carbon tetrachloride and alcohol, while benzene and carbon tetrachloride do not. Two liquid layers do not occur with any pair or with the three. The author has made an exhaustive study of the corresponding pressures and temperatures for all possible mixtures of the three components and has discussed his results at length. There is no minimum boiling-point for the ternary system. W. D. B.

**On soap solutions.** *A. Smits. Zeit. phys. Chem.* 45, 608 (1903). — A solution of sodium palmitate,  $M/1$ , has the same boiling-point and freezing-point as pure water and is therefore a colloidal solution. Owing to hydrolysis a more

dilute solution has a different vapor pressure from that of pure water. It is not quite clear why addition of a substance which does not dissolve should force the hydrolytic dissociation back to zero. *W. D. B.*

**Action of carbonic anhydride on the metal-ammoniums.** *É. Rengade. Comptes rendus, 138, 629 (1904).* — Below  $-50^{\circ}$  carbon dioxide reacts with sodium ammonium and potassium ammonium, forming carbamate and setting free hydrogen. At a little higher temperature formate is also formed. *W. D. B.*

**Direct hydrogenization of the homologues of aniline.** *P. Sabatier and J. B. Senderens. Comptes rendus, 138, 1257 (1904).* — Methyl aniline and ethyl aniline form hydrogen addition-products readily when passed over pulverulent nickel at  $160^{\circ}$ – $180^{\circ}$ . Metatoluidine forms hydrogen addition-products with great difficulty, apparently because the substances thus formed are not very volatile and condense on the nickel, destroying its catalytic action. *W. D. B.*

**New studies on the cementation of carbon steels and special steels.** *L. Guillet. Comptes rendus, 138, 1600 (1904).* — The rate of cementation with carbon depends on the carbonate present and not on the nitrogen in the atmosphere. Elements which form double carbides with iron and carbon appear to increase the rate of cementation, while the contrary is the case for metals which dissolve in the iron. Carbon is taken up by  $\gamma$ -iron at ordinary temperatures. *W. D. B.*

**The decomposition by heat of a mixture of calcium carbonate and an alkali carbonate.** *P. Lebeau. Comptes rendus, 138, 1496 (1904).* — The dissociation pressures for a mixture of calcium and caesium carbonates are said to lie between those of the two single salts. Since the residue is said to be pure lime, this statement is probably inaccurate. Similar results were obtained with mixtures of calcium carbonate with sodium, potassium, or rubidium carbonate. From the article it is impossible to tell what actually happened. *W. D. B.*

**The variable hydrolytic equilibrium with dissolved chromium sulphate.** *T. W. Richards and F. Bonnet. Zeit. phys. Chem. 47, 29 (1904).* — Diffusion, migration, inversion and precipitation experiments with the chromium sulphates favor the view that the violet solutions contain the normal sulphate while the green solution is due to the presence of a green basic salt in which at least 47 percent of acid radical has been replaced by hydroxyl. The acid set free appears to be sulphuric acid and not a complex acid. There may of course be several green basic salts. *W. D. B.*

**Occlusion during coagulation.** *J. Duclaux. Comptes rendus, 138, 571, 809 (1904).* — The author believes that the substances carried down when a solution coagulates are due to "simple substitutions of the radicals composing the precipitating salt for those of the colloid." Since no figures are given it is a little difficult to tell just what the author means, and quite impossible to tell whether he has proved his case. *W. D. B.*

**The coagulation of colloidal solutions.** *J. Duclaux. Comptes rendus, 138, 809 (1904).* — The author looks upon "coagulation as resulting from a certain change of composition, a change which can be brought about by addition of a suitable quantity of any salt." *W. D. B.*

*Osmotic Pressure and Diffusion*

**Diffusion and supersaturation in gelatine.** *H. W. Morse and G. W. Pierce. Proc. Am. Acad.* 38, 625; *Zeit. phys. Chem.* 45, 589 (1903). — This is a study of Liesegang's experiment in which a drop of silver nitrate on a gelatine impregnated with potassium chromate caused precipitation of silver chromate in concentric rings. The experiments of the authors were made with a vertical rod of gelatine dipping into a silver nitrate solution. The authors measured the times at which the discs appeared and the distances between the discs. From these data they conclude "that there exists in the case of the formation of silver chromate in gelatine solution a definite constant product  $Ag^2 \times CrO_4 = \text{constant}$ , which determines the limit of supersaturation with respect to silver chromate in the absence of the solid phase." *W. D. B.*

**On the limits of sensibility of odors and emanations.** *M. Berthelot. Comptes rendus*, 138, 1249 (1904). — It takes an hour for iodoform to volatilize into a volume of 100 cc to such an extent that iodoform can be detected by the nose in a 1 cc sample of air. If the 100 cc flask were replaced every hour by a fresh one, the iodoform would lose less than one milligram in one hundred years. With musk a hundred thousand years would probably be necessary. The bearing of this on any discussion of emanations is obvious. *W. D. B.*

*Velocities*

**Theory of reaction velocity in heterogeneous systems.** *W. Nernst. Zeit. phys. Chem.* 47, 52 (1904). — This article forms an introduction to Brunner's research, reviewed below. The theory is an extension of the principle, first enunciated by Noyes and Whitney for the case of the solution of a solid in a liquid, that, at the boundary between a liquid and a solid, equilibrium is immediately established. When the reaction taking place in the liquid itself is sufficiently rapid, the rate of the reaction between the two phases will depend only on the velocity with which the differences in concentration at the surface of the solid and in the body of the liquid tend to become equalized. With sufficiently energetic stirring the change in concentration may be restricted to a thin film of liquid adhering to the surface of the solid, the thickness of which may be determined from the rate of solution and the diffusion constant of the solute. *F. B. K.*

**Reaction velocity in heterogeneous systems.** *E. Brunner. Zeit. phys. Chem.* 47, 56 (1904). — The various conclusions from the above theory (previous review) are tested experimentally. In all the experiments the same area of surface and the same vessel and stirrer were used. The measurements were carried out mostly at 20° and 30°. The velocity of a reaction in which a dissolved substance takes part, which cannot exist in appreciable concentration at the surface of the solid, must be proportional to the concentration of this substance, provided the diffusion constant remains unchanged during the process. Consequently the velocity should be independent of the nature of the solid material. This conclusion is verified in the case of the solution of magnesium, basic magnesium carbonate and magnesias, all of which dissolve with about the same velocity in benzoic acid solution. In hydrochloric acid,

magnesium and magnesia dissolved with the same velocity, but marble gave a rate about 50 percent too high.

Similarly, the rates of electrolytic separation of hydrogen, from benzoic acid and from hydrochloric acid, on the platinized platinum electrode, were independent of the cathode potential, between certain limits, and were, moreover, the same as the rates of solution of equivalent quantities of magnesia in the same acids.

Another important conclusion from the theory is that the rate of solution of a substance in water must be the same as the rate of reaction of the saturated solution of this substance with any solid at whose surface the concentration of the other material is very low. This was also verified by the following results. (1) The rate of solution of benzoic acid agreed roughly with the rate of solution of magnesium and magnesia in benzoic acid. (2) The rate of solution of solid iodine and the rate of electrolytic reduction of iodine by a platinum cathode under similar conditions stood in the ratio of 3 to 4, which the author considers a good agreement, in view of the irregularities in the solution of the iodine.

Although many of the results are vague and unsatisfactory, the main points of the theory appear to be on the whole substantiated.

The appearance of the article is marred by the use of unnecessary and annoying abbreviations in the text. The occurrence of such expressions as "salzkz," "kzverteilung" and "N. and W." (Noyes and Whitney) do not add to the pleasure of reading.

F. B. K.

**Theory of catalytic reactions.** *H. Euler. Zeit. phys. Chem.* 47, 353 (1904). — A protest against the claim that Kullgren (7, 547) was the first to prove that the change of the reaction velocity with changing temperature is due chiefly to a change in the dissociations of the reacting substances.

W. D. B.

**A dynamical study of the Friedel-Crafts reaction.** *B. D. Steele. Jour. Chem. Soc.* 83, 1470 (1903). — The ketone synthesis from toluene and benzoyl chloride and the hydrocarbon synthesis from toluene and benzyl chloride in the presence of aluminium chloride and of ferric chloride were studied. The following conclusions were arrived at. When the ratio of aluminium chloride to acid chloride is not greater than unity the reaction between benzoyl chloride is monomolecular and "the mechanism suggested by Perrier and Boeseken is well established." "In the presence of excess of aluminium chloride, the reaction is best explained as being bimolecular, the reacting species being two intermediate compounds, each containing aluminium chloride." In the presence of ferric chloride the reaction is bimolecular, the same explanation being given as in the previous case. "In the synthesis of phenyltolylmethane from toluene and benzyl chloride in the presence of aluminium chloride, the reaction is monomolecular, and is probably one between toluene and a compound of aluminium and benzyl chlorides, and the same applies to the reaction in the presence of ferric chloride."

F. B. K.

**The velocity and mechanism of the reaction between potassium ferricyanide and potassium iodide in aqueous solution.** *F. G. Donnan and R. Le Rossignol.*



*Jour. Chem. Soc.* 83, 703 (1903). — The authors have used the compensation method in determining the rate of oxidation of potassium iodide by potassium ferricyanide, at 34.7°. When the same initial concentration of ferricyanide was used the rate was very closely proportional to the square of the concentration of the ferricyanide and the cube of that of the iodide. The authors noted however a very curious dependence of the velocity constant on the total concentration of ferrocyanide *plus* ferricyanide, that is, on the initial concentration of the ferricyanide when no ferrocyanide was added. The assumption that the rate is determined by a reaction between the K'-ion and the minute amount of Fe...-ion, and that the ferrocyan-ion and ferricyan-ion are equally dissociated, leads to a good quantitative interpretation of all the results. *F. B. K.*

**On the rate of decomposition of carbon monoxide.** *A. Smits and L. K. Wolff. Zeit. phys. Chem.* 45, 199 (1903). — In the presence of reduced nickel, carbon monoxide changes to carbon dioxide with separation of carbon. The rate of change was measured manometrically at 25°, 310°, 340° and 445° and the reaction found to be approximately monomolecular. At the latter temperature the reverse reaction takes place to an appreciable extent. It is pointed out that Schenck and Zimmermann, who found the same reaction to be bimolecular at the higher temperatures, had overlooked the fact that the nickel loses its activity during the process owing to a protecting layer of deposited carbon. The present authors used nickel which had been brought to a state of practically constant activity by a thorough coating of carbon before the beginning of the reaction. *F. B. K.*

**Study on the law of action of maltase.** *E. F. Terroine. Comptes rendus*, 138, 778 (1904). — The rate of hydrolysis of maltose in presence of maltase can be expressed by the formula

$$v = k \frac{a}{1 + ma},$$

where  $v$  is the rate of hydrolysis,  $a$  the concentration of maltose,  $k$  and  $m$  constants depending on the conditions of the experiment and on the ferment. This is the same formula that holds for invertine, emulsine, amylase and trypsin.

*W. D. B.*

**Studies on the action of maltase.** *C. Philoche. Comptes rendus*, 138, 779 (1904). — This is a preliminary study of the action of maltase on glucose. The maltase was the Taka diastase. The catalytic action of the maltase does not change during twenty-four hours' action at 40°, so that one is justified in considering the ferment as remaining unchanged. *W. D. B.*

**Action of hydriodic acid on the oxidation of sulphurous acid.** *A. Berg. Comptes rendus*, 138, 907 (1904). — "The concentration of hydriodic acid determines whether it accelerates or retards the oxidation of sulphurous acid. For each solution of sulphurous acid there appears to be a concentration of hydriodic acid which does not affect the rate of oxidation. For 4 percent solutions the concentration is about 3 percent, which corresponds very nearly to one molecular weight of hydriodic acid to three of sulphurous acid.

"Hydriodic acid is not the only substance which accelerates the oxidation

of sulphurous acid. In this same class come manganese chloride and ferrous chloride, which is in harmony with the oxidizing action of these salts on organic compounds. The soluble metallic iodides act in the same way.

"On the other hand the chloride and bromide of potassium have no action. Hydrochloric acid decreases the rate, bringing the reaction to a standstill when present in large quantities."

There is nothing in this paper to show that the author has ever heard of Lothar Meyer, Bigelow, and others. W. D. B.

On the rate of decomposition of ammonium nitrite, II. *K. Arndt. Zeit. phys. Chem.* 45, 571 (1903). — This is mainly a criticism of Blanchard's article on the same subject (*Zeit. phys. Chem.* 41, 681 (1902)). Incidentally a determination of the dissociation constant of nitrous acid is made. F. B. K.

On the solution of metals, II. *T. Ericson-Aurén and W. Palmaer. Zeit. phys. Chem.* 45, 182 (1903). — The authors bring forward further evidence in favor of the theory of "local currents" for the solution of metals in acids. F. B. K.

The disappearance of radio-activity induced on solids by radium. *P. Curie and J. Danne. Comptes rendus*, 138, 683, 748 (1904). — If the radium emanation produces a substance B in the solid on which the emanations act and if this substance B changes according to an exponential formula into a substance C which also disappears according to an exponential formula, we can write an equation for the rate of the change on the assumption that both B and C are radioactive or that C alone is radioactive. The experiments seem to show that C alone is radioactive and that B disappears faster than C. At higher temperatures, disturbing factors appear. W. D. B.

Emission of water vapor by plants. *M. Berthelot. Comptes rendus*, 138, 16 (1904). — Plants dried in the air were found to lose more water at 110°. The author draws the extraordinary conclusion that the water therefore existed in two different states. From the rate of loss in the air, the author concludes that he is studying an irreversible reaction. The reviewer sees nothing in the data which warrants this conclusion and the conclusion was not checked in any way. W. D. B.

The oxidizing action of manganous salts in presence of a colloid. *A. Trillat. Comptes rendus*, 138, 274 (1904). — Certain colloids prevent the precipitation of manganous salts by an alkali. Such non-precipitated alkaline solutions possess remarkable oxidizing powers. W. D. B.

#### *Electromotive Forces*

Action of radium bromide on the electrical resistance of bismuth. *R. Paillet. Comptes rendus*, 138, 139 (1904). — The radiation from radium bromide decreases the electrical resistance of bismuth. W. D. B.

#### *Electrolysis and Electrolytic Dissociation.*

Physical-chemical studies on the so-called explosive antimony. *E. Cohen and W. E. Ringer. Zeit. phys. Chem.* 47, 1 (1904). — When a hydrochloric

acid solution of antimony trichloride is electrolyzed, the precipitated antimony always contains antimony trichloride which is apparently not mechanically included. The amount of  $\text{SbCl}_3$  in the precipitated antimony is practically independent of the hydrochloric acid solution, decreases slightly with increasing current density, decreases markedly with rising temperature, and increases very much with increasing antimony trichloride concentration. For a solution containing 85.7 percent antimony trichloride, a metal was obtained containing 10.5 percent trichloride. Antimony containing less than 4.5 percent antimony trichloride appears not to be explosive. The data seem to point to the existence of two series of solid solutions. In the first the metal contains 0-1.8 percent of antimony trichloride and is non-explosive. In the second series the metal contains 4.5-10.5 percent trichloride and is explosive. The paper is a preliminary one and does not deal with the theory of explosive antimony.

W. D. B.

The importance of the cathode material for the electrolytic reduction of nitrobenzene. W. Löb and R. W. Moore. *Zeit. phys. Chem.* 47, 418 (1904). — Since we get the same reduction with a copper cathode as with a platinum cathode plus a copper salt in spite of the fact that no copper is precipitated in the second case, it is obvious that the copper cathode cannot be treated as a non-attackable electrode. Experiments with a number of different metals as cathode showed that when the cathode potential was kept constant, the same products, azoxybenzene and aniline, were formed in each case and to practically the same extent. The cathode potential is therefore the determining factor in the case of electrolytic reductions with different cathodes.

W. D. B.

On electrical reduction. F. Haber and R. Russ. *Zeit. phys. Chem.* 47, 257 (1904). — In a previous paper (4, 551) Haber deduced a formula for the electrolytic reduction of nitrobenzene which agreed with the facts when multiplied by an arbitrary constant. It is now shown that this arbitrary constant is a function of the nature of the electrode and of its previous history. The variations are connected with the absorption of gas or the formation of gas films. There is an experimental study of quinone, quinhydrone and hydroquinone; also of iodine and hydriodic acid. The authors protest against the assumption that a reaction which takes place slowly in a homogeneous system will necessarily take place instantaneously if the solution happens to be saturated with respect to one of the reacting substances.

W. D. B.

Electrolytic separation of nickel and zinc. A. Hollard and Bertiaux. *Comptes rendus*, 138, 1605 (1904). — Ammonia, magnesium sulphate, sulphuric acid, ammonium nitrate, and  $\text{SO}_2$  are added to a solution of zinc and nickel sulphates. The ostensible reason for this is to form nitrite, but it would seem more rational to have added nitrite direct. This solution is electrolyzed at  $85^\circ$ , all the nickel precipitating and none of the zinc.

W. D. B.

New method of making calcium carbide. H. Moissan. *Comptes rendus*, 138, 661 (1904). — When fused calcium chloride is electrolyzed at a red heat with a graphite cathode, small amounts of carbide are formed. When calcium fluoride and coke are added to the bath, carbide is formed even at  $650^\circ$ .

W. D. B.

**Electrical osmose in methyl alcohol.** *A. Baudouin. Comptes rendus*, 138, 898, 1165 (1904). — To produce a given rate of electrical endosmose a higher voltage is necessary with methyl alcohol than with water. The sign of the flow depends on the nature of the diaphragm and on the substances dissolved in the alcohol. *W. D. B.*

**The effect of complex ions on electrolysis with alternating currents.** *A. Brochet and J. Petit. Comptes rendus*, 138, 419 (1904). — Cases are cited in which no complex ion is formed and yet there is electrolysis with alternating currents. More interesting than these are the rapid rates at which iron, cobalt and platinum dissolve in cyanide solutions. The cobaltocyanide is instable and changes to cobaltcyanide with evolution of hydrogen. *W. D. B.*

**Electrolytic dissolving of platinum.** *A. Brochet and J. Petit. Comptes rendus*, 138, 1095 (1904). — Platinum does not dissolve at all when made anode in a potassium cyanide solution, direct current being used. With a concentrated potassium cyanide solution, an alternating current with a frequency of forty-two, and a current density of 80 amp/qdm, platinum dissolves readily, the current efficiency being about fifteen percent. With hydrochloric acid the current efficiency is only one percent. *W. D. B.*

**Remarks on the use of alternating currents in chemistry and on the theory of the reactions thus caused.** *M. Berthelot. Comptes rendus*, 138, 1130 (1904). — The author believes that water is electrolyzed when an alternating current passes through a solution and that the dissolving of platinum in cyanide solutions (preceding review) is due to the oxidation of the platinum. *W. D. B.*

**Effect of frequency in electrolysis with alternating currents.** *A. Brochet and J. Petit. Comptes rendus*, 138, 1421 (1904). — It has been believed that the current efficiency decreased continuously with increasing frequency of alternation. This however cannot be true if the yield is zero with a direct current and not zero with an alternating one. With cobalt and nickel in a potassium cyanide solution, there is a maximum efficiency at about 15 cycles for cobalt and about 25 cycles for nickel. With platinum the efficiency is practically independent of the frequency between 40 and 100 cycles. *W. D. B.*

**Direct study of the transfer of ultramicroscopic particles by the microscope.** *A. Cotton and H. Moulon. Comptes rendus*, 138, 1584 (1904). — The authors have watched the electrical transference of colloidal silver under the microscope. At the surface of the liquid the particles move to the anode. In the film next to the glass the particles move in the opposite direction. With a quartz vessel this effect is less marked and it is zero with a gypsum wall. When an alternating current is applied to a colloidal silver solution, the bright particles lengthen out into a line under the microscope. *W. D. B.*

**The conductivity of mixtures of electrolytes.** *F. Barmwater. Zeit. phys. Chem.* 45, 557 (1903). — The conductivities of mixtures of acetic and glycollic acids can be calculated from the conductivities of the single acids. With other pairs the agreement was not so good. *W. D. B.*

Can one detect formation of complexes from the electrolytic conductivity of mixed acids? *R. Hofmann. Zeit. phys. Chem.* 45, 584 (1903). — When two acids form complex substances it is impossible to find concentrations which shall follow the law of isohydric solutions even approximately. This case is realized with mixtures of hydrochloric and chromic acids. *W. D. B.*

On the apparent decrease in energy of a weak acid in presence of a neutral salt of this acid. *G. Chesneau. Comptes rendus*, 138, 968 (1904). — Zinc acetate, manganese acetate and acetone decrease the action of acetic acid on zinc more than does sodium acetate, even though this last salt is the most dissociated of the four substances. The action of sodium acetate in preventing the action of hydrogen sulphide on nickel acetate is attributed to the formation of sodium sulphide. It is not stated why sodium sulphide should not react with nickel acetate. *W. D. B.*

#### Dielectricity and Optics

Dielectric cohesion of argon and its mixtures. *E. Bouty. Comptes rendus*, 138, 616 (1904). — The dielectric cohesion of argon is only 30, much lower than that of hydrogen. Presence of traces of other gases causes a marked increase. *W. D. B.*

On freshly prepared gases. *E. Bloch. Comptes rendus*, 138, 1599 (1904). — Most chemically-prepared gases are at first conductors of electricity and are usually charged positively or negatively. "The ions, to which the freshly-prepared gases owe their conductivity, appear to resemble in their properties (migration and condensation), the emanations from phosphorus and from electrolytic gases. They form a new category distinct from ordinary ions." It is believed that the condensation of water vapor on these ions is independent of the electrical charge and that the two properties referred to are really due to different causes. *W. D. B.*

Thermal ionization of salt vapors. *G. Moreau. Comptes rendus*, 138, 1268 (1904). — When the vapor of a salt solution is heated to say 1000°, its conductivity is increased and this new conductivity remains to a certain extent when the vapor is cooled. The most marked effects are obtained with potassium salts, the iodide, chloride, bromide, and nitrate being the best among these. *W. D. B.*

Emanations and radiations. *M. Berthelot. Comptes rendus*, 138, 1553 (1904). — It is urged that we should not be over hasty in imagining new hypotheses to explain so-called emanations and radiations. The amount of arsenic emitted from wall-papers is of the same order as some of the emanations. No balance can detect the amount of musk which is perceived readily by the nose. The amount of hydrogen or oxygen necessary to polarize an electrode is very small. Tyndall's experiments on dust show how pertinaciously air retains solid particles. In view of these facts the author thinks it probable that many of the phenomena of emanation and radiation are chemical phenomena in the strict sense. *W. D. B.*

The radioactivity of the gases from thermal springs. *P. Curie and A. La-*

*borde. Comptes rendus*, 138, 1150 (1904). — It is found that the gases from many of the well-known thermal springs are radioactive and that they lose their radioactivity to a very considerable extent on standing. This will be hailed with delight by the proprietors of these springs as establishing that the water drunk at the spring has health-giving powers which cannot be equaled by chemical counterfeits.

W. D. B.

**Microscopic state of the poles, and the discharge spectra.** *B. Eginitis. Comptes rendus*, 138, 1208 (1904). — When an arc plays between poles of nickel, platinum, iron or manganese, a number of bright points form on the ends of the poles. Each bright point seems to be a centre emitting incandescent vapors. These points "appear to be true microscopic craters scattered over a length which varies with the nature of the poles, their form, the distance between them, the self-induction of the circuit, etc." With lead and tin as electrodes, one sees drops which are due to fusion and which disappear when they reach the point where the arc is striking.

W. D. B.

**The comparability of spectrophotometric determinations.** *P. Vaillant. Comptes rendus*, 138, 1088 (1904). — In a quantitative spectrophotometric study of colored solutions, the comparisons refer to a small section of the spectrum and not to a single wave-length. It is shown that this may introduce serious errors when the absorption of the solution varies markedly with the wave-length. Paranitrophenol is cited as a case where the absorption coefficient doubles when the wave-length changes from 520 to 510  $\mu$ .

W. D. B.

**The rotation and dispersion in solutions, II.** *C. Winther. Zeit. phys. Chem.* 45, 331 (1903). —

1. The maximum temperatures in the temperature equations for specific rotations is practically independent of the wave-length and the concentration.
2. The 'rational dispersion coefficient' is constant throughout the whole tartaric acid group.
3. With substances showing anomalous dispersion the changes in rotation and dispersion are so connected that the same change of rotation causes practically the same change of dispersion regardless whether this is brought about by varying the temperature or the concentration.
4. The change of the dispersion with the concentration is nearly independent of the absolute concentration and can therefore be expressed by a constant, the solution dispersion coefficient.
5. This solution dispersion coefficient depends both on solvent and solute.

W. D. B.

**The refractive powers of dissolved substances.** *C. Chéneveau. Comptes rendus*, 138, 1483, 1578 (1904). — For aqueous solutions the author finds that the refractive index of the solute may be considered as the sum of a term due to the basic radical and of a term due to the acid radical. It is claimed that this result is independent of the degree of dissociation; but the experiments of others make it probable that this conclusion is due to experimental error.

W. D. B.

**On cacodylic acid and amphoteric substances.** *P. T. Muller and E. Bauer.*

*Comptes rendus*, 138, 1099 (1904). — A study of the molecular refraction of cacodylic acid leads the authors to the conclusion reached by Hantzsch (8, 456) that Zawidski was wrong in calling cacodylic acid a pseudo-acid. *W. D. B.*

The spectrum of calcium fluoride. *C. Fabry. Comptes rendus*, 138, 1581 (1904). — When an arc passes between cored carbons containing calcium fluoride a brilliant band spectrum is obtained which is apparently due to undecomposed calcium fluoride. The lines in each band can be represented by a formula of the type

$$N = B - Am^2,$$

where  $N$  is the inverse of the wave-length,  $B$  and  $A$  are constants, and  $m$  is a whole number representing the number of the line. *W. D. B.*

On the flame spectra of the alkali metals. *C. de Walleville. Comptes rendus*, 138, 346 (1904). — If the whole flame be so focussed that its image is no longer than the slit of the spectroscope, the spectrum is divided into three bands, containing different lines and apparently corresponding to different temperatures. *W. D. B.*

The absorption spectra of didymium solutions containing phosphoric acid. *A. Waegner. Ber. chem. Ges. Berlin*, 36, 3055 (1903). — If phosphoric acid be added to a didymium chloride solution, the character of the absorption spectrum is changed. Data are given showing the nature of the change. On heating or diluting these solutions, didymium orthophosphate precipitates.

*W. D. B.*

The effect of temperature on the specific rotation of strongly optically-active substances. *H. Grossmann and H. Potler. Ber. chem. Ges. Berlin*, 37, 84 (1904). — With rising temperature the specific rotation of ammonium molybdanyl bimalate first increases, passing through a maximum at about  $35^\circ$ , and then decreases. With increasing dilution at constant concentration, there is a decrease in specific rotation, but this is not very marked. *W. D. B.*

An asymmetric synthesis. *W. Marckwald. Ber. chem. Ges. Berlin*, 37, 349 (1904). — By asymmetric synthesis is meant the synthesis of a substance containing an asymmetric carbon under such conditions that there shall be formed an excess either of the dextrorotary or of the lævorotary compound. The author has now made the first synthesis of this class by heating the acid brucine salt of methyl ethyl malonic acid. Carbonic acid is evolved and the valerianic acid formed contains a ten percent excess of lævorotary valerianic acid.

*W. D. B.*

Chemical action of light. *M. Berthelot. Comptes rendus*, 138, 1297 (1904). — In the dark, gold and platinum are not attacked by fuming hydrochloric acid even in presence of manganous chloride. Both metals are attacked by the pure acid when exposed to the light. Manganous chloride accelerates the action.

*W. D. B.*

The color-sensitive silver chloride. *E. Baur. Zeit. phys. Chem.* 45, 613 (1903). — The author has repeated and extended the experiments of Wiener on the silver photochloride which assumes the color of the light falling upon it.

After the color has been produced there is no perceptible change in the dark. It is believed that we are dealing with a continuous series of solid solutions in which  $\text{AgCl}$  and  $\text{Ag}_2\text{Cl}$  are the end terms. *W. D. B.*

**A new method of photographing in colors.** *A. and L. Lumière. Comptes rendus*, 138, 1337 (1904). — A glass plate is covered with a single layer of transparent grains, consisting of a mixture of orange-red, green and violet particles. A photographic film is flowed over the plate, the exposure made from the back and a positive developed. By transmitted light one gets a photograph in colors because the reduced silver cuts off the light from certain particles. There must be great experimental difficulties in preparing such a plate, but the authors claim that these have been overcome. The spaces between the transparent grains are filled with lamp-black. *W. D. B.*

**The action of magnetic fields on phosphorescent substances.** *C. Gutton. Comptes rendus*, 138, 568 (1904). — "Every time that changes in the intensity of a magnetic field or displacements of the lines of force cause electromotive forces in the place where there is a phosphorescent sulphide, there is an increase in the phosphorescence." *W. D. B.*

**The action of magnetism on phosphorescence.** *A. de Hemptinne. Comptes rendus*, 138, 754 (1904). — The author has repeated Gutton's experiments (preceding review) and has not been able to detect any change in phosphorescence due to a change in the magnetic field. Since Gutton's calcium sulphide phosphoresced with a violet light, and the author's with a greenish-yellow light, the author believes that the discrepancy may be due to a difference in samples. An interchange of samples would appear to be the proper thing. *W. D. B.*

**Effect of certain chemical and osmotic phenomena on phosphorescence.** *M. Lambert. Comptes rendus*, 138, 626 (1904). — The diffusion of a salt solution through parchment paper is said to increase the phosphorescence of a sulphide screen placed in (or near?) the more dilute solution. *W. D. B.*

#### *Crystallography, Capillarity and Viscosity*

**On a capillarmeter.** *E. Tassilly and A. Chamberland. Comptes rendus*, 137, 645 (1903). — The apparatus consists essentially of a biconcave cylindrical lens, on the two plane surfaces of which two parallel plates are fastened. This is placed in the liquid and the differences in level of the two menisci are determined. The authors believe that the simplicity of the apparatus and the advantages of a differential reading make the "capillarmeter a very serviceable instrument." *W. D. B.*

**The hydrates of ethyl alcohol.** *E. Varenne and L. Godefroy. Comptes rendus*, 137, 993 (1903); 138, 79 (1904). — From the change of the viscosity coefficient of aqueous alcohol with the concentration, the authors deduce the certain existence of the hydrates  $\text{C}_2\text{H}_5\text{OH} \cdot 2\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_5\text{OH} \cdot 3\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_5\text{OH} \cdot 6\text{H}_2\text{O}$  and the probable existence of the hydrates  $3\text{C}_2\text{H}_5\text{OH} \cdot 2\text{H}_2\text{O}$  and  $\text{C}_2\text{H}_5\text{OH} \cdot 22\text{H}_2\text{O}$ . The apparatus used is described in detail in the second paper. *W. D. B.*

**The hydrates of methyl alcohol and acetone.** *E. Varenne and L. Godefroy. Comptes rendus*, 138, 990 (1904). — Viscosity determinations for methyl



alcohol and water show a maximum viscosity for one mixture. The same is true for mixtures of acetone and water. From the data the authors deduce the existence of the compounds of methyl alcohol containing one, two, three, five, eight and twenty of water, while acetone is believed to combine only with three, four, eight, and probably thirty-four of water. *W. D. B.*

On suspensions in media with high internal friction. *A. Müller. Ber. chem. Ges. Berlin*, 37, 11 (1904). — Experiments on the precipitation of colloidal gold or colloidal red phosphorus by electrolytes show that substances which increase the viscosity of the solution decrease the rate of precipitation. *W. D. B.*

On the properties of systems showing hysteresis and viscosity. *P. Duhem. Comptes rendus*, 138, 942 1075 (1904). — In Marchis's experiments on thermometers and in Chevallier's experiments on the resistance of platinum-silver alloys, slight oscillations of temperature had a marked effect in decreasing the time necessary to reach equilibrium. In some other experiments slight oscillations had little or no effect on the time necessary to reach equilibrium. This second state of affairs occurs when "the coefficient of viscosity is large in comparison with the oscillation in the value of the observable action." Instances to which this applies are to be found in the work of Bonasse on soft metals and on vulcanized rubber; also in some of van Bemmelen's work on the hydration of gelatinous precipitates. *W. D. B.*

Separation of solids in the surface layers of solutions and suspensions. *W. Ramsden. Zeit. phys. Chem.* 47, 336 (1904). — The author has found that films of solid or very viscous matter form at the free surfaces and inter-surfaces of many colloid solutions or suspensions. The bearing of this on many matters is discussed at length. *W. D. B.*

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# ON THE MOLECULAR DEPRESSION OF THE FREEZING-POINT OF WATER PRODUCED BY SOME VERY CONCENTRATED SALINE SOLUTIONS

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BY L. C. DE COPPET

Several years before Raoult first took up the subject of congelation, I had published the results of numerous experiments on the molecular-depression of the freezing-point of aqueous saline solutions.<sup>1</sup>

I made no experiments with very dilute solutions. Thus it happened that the decrease in the molecular depression with increasing concentration, which seems to be common to all electrolytes in very dilute aqueous solutions, and which was first noticed by Raoult, escaped my observation.

On the other hand I determined the freezing-points of very concentrated, and in *some* cases of *highly supersaturated* solutions. These experiments have never been repeated by any subsequent investigator, and I desire to call attention to them in connection with a paper recently published by H. C. Jones and F. H. Getman, entitled: *The molecular-lowering of the freezing-point of water produced by concentrated solutions of certain electrolytes.*<sup>2</sup>

The object of the researches of Jones and Getman was to ascertain whether the *minimum* in the molecular-lowering of the freezing-point which has been observed in many cases "*is at all general, or whether it is limited to certain substances or certain classes of closely related substances.*"<sup>3</sup>

---

<sup>1</sup> Ann. Chim. Phys. (4) 23, 366 (1871); 25, 502; 26, 98 (1872). Bulletin de la Société vaudoise des Sciences naturelles, 10, 535 (1871); 11, 7 (1872). I was the first to make use of the expression *molecular* or *atomic* depression of the freezing-point.

<sup>2</sup> Zeit. phys. Chem. 46, 244 (1903).

<sup>3</sup> loc. cit. 244.

Jones and Getman furthermore enquire: "*How long will the molecular-lowering (produced by the substances for which there is a minimum) continue to increase as we increase the concentration, and what magnitude will it acquire in very concentrated solutions of very soluble electrolytes.*"<sup>1</sup>

For a number of salts, my experiments furnish a reply to these questions.

In the following tables, which contain extracts, in modernized form, from my former publications, the symbols employed have the following significance:

$m$  = concentration in gram-molecular normal.<sup>2</sup>

$m'$  = concentration in gram-molecules to 1000 grams water.

$\Delta$  = freezing-point depression. The sign \* indicates that the solution is supersaturated at the temperature at which it freezes.<sup>3</sup>

$$\frac{\Delta}{m} \text{ (or } \frac{\Delta}{m'} \text{)} = \text{molecular freezing-point depression.}^4$$

The freezing temperatures observed by me are lower than those found by Jones and Getman. This might be attributed in part to my not having taken into account the increase in concentration due to the separation of ice. On the other hand, my solutions were in open beaker vessels, exposed to the warmer

<sup>1</sup> loc. cit. 251.

<sup>2</sup> The tables of specific gravity of Kohlrausch, Gerlach, Kremers and Schiff were used for calculating  $m$ . In some cases extrapolation was necessary.

<sup>3</sup> The temperature estimation, except in the case of some of the less concentrated solutions, was not usually carried beyond 1/40 degree. The two very good thermometers used had been constructed by Greinert in Munich in view of these experiments.

From 100 to 300 grams solution were used for each experiment. In the case of supersaturated solutions only this quantity was reduced to from 30 to 60 grams. The process used for determining the freezing-point of supersaturated solutions is described in Ann. Chim. Phys. (4) 23, 403 (1871) and in Bull. Soc. vaud. Sc. nat. 11, 23 (1872).

<sup>4</sup> The question as to whether the molecular-depression is best expressed by  $\Delta/m$  or by  $\Delta/m'$  has been discussed by Abegg in Zeit. phys. Chem. 15, 248 (1894).

air of the laboratory, and to the condensation of moisture on the surface of the solution. Both these sources of error tend to raise the apparent freezing-temperature.

Potassium carbonate,  $K_2CO_3$ , (138.3)

$m$	$m'$	$\Delta$	Loomis <sup>1</sup>	$\frac{\Delta}{m}$	de Coppet <sup>3</sup>	$\frac{\Delta}{m'}$
				Jones <sup>2</sup>		de Coppet
0.05	—	—	4.710	4.75	—	—
0.06	—	—	—	4.75	—	—
0.10	—	—	4.540	4.62	—	—
0.20	—	—	4.385	—	—	—
0.40	—	1.683	—	4.208	—	—
0.43	0.43	1.90	—	—	4.42	4.42
0.54	0.54	2.40	—	—	4.44	4.44
0.71	0.72	3.20	—	—	4.51	4.44
0.85	0.87	3.85	—	—	4.53	4.43
0.99	1.01	4.55	—	—	4.60	4.50
1.00	—	4.375	—	4.375	—	—
1.27	1.30	6.00	—	—	4.72	4.61
1.40	1.45	6.75	—	—	4.82	4.66
1.64	1.71	8.25	—	—	5.03	4.82
1.73	1.81	8.85	—	—	5.12	4.89
2.00	—	9.710	—	4.855	—	—
2.05	2.17	11.15	—	—	5.44	5.14
2.66	2.89	16.7	—	—	6.28	5.78
3.23	3.62	23.45	—	—	7.26	6.48
3.78	4.34	31.6	—	—	8.36	7.28

The general trend of the results is none the less manifest. There is a *minimum* in the molecular-lowering for  $m = 0.4$ , or thereabouts.  $\frac{\Delta}{m'}$  scarcely varies from  $m' = 0.4$  to 0.9, after which both  $\frac{\Delta}{m}$  and  $\frac{\Delta}{m'}$  increase continuously as the concentration increases. They both attain values which have no meaning when viewed from the standpoint of the theory of electrolytic dissociation.

<sup>1</sup> Phys. Rev. 3, 276 (1896). (Cited by Jones.)

<sup>2</sup> loc. cit. 276.

<sup>3</sup> Ann. Chim. Phys. (4) 25, 528 (1872).

Ammonium nitrate,  $\text{NH}_4\text{NO}_3$ , (80.12)

$m$	$m'$	$\Delta$	Loomis <sup>1</sup>	$\frac{\Delta}{m}$	de Coppet <sup>2</sup>	$\frac{\Delta}{m'}$
				Jones <sup>3</sup>		de Coppet
0.025	—	—	3.49	—	—	—
0.050	—	—	3.47	—	—	—
0.100	—	—	3.424	—	—	—
0.200	—	—	3.321	—	—	—
0.25	0.25	0.83	—	—	3.32	3.32
0.50	—	1.686	—	3.372	—	—
0.60	0.62	2.03	—	—	3.34	3.27
0.72	0.75	2.40	—	—	3.33	3.20
1.00	—	3.145	—	3.145	—	—
1.17	1.25	3.85	—	—	3.29	3.08
1.40	1.50	4.55	—	—	3.25	3.03
2.00	—	5.996	—	2.998	—	—
2.23	2.50	6.90	—	—	3.09	2.76
3.00	—	8.720	—	2.906	—	—
3.16	3.75	9.35	—	—	2.96	2.49
4.01	4.99	11.75	—	—	2.93	2.35
4.73	6.24	13.6	—	—	2.88	2.18
5.46	7.49	15.6	—	—	2.86	2.08
6.10	8.77	17.4	—	—	2.85	1.98

I found the eutectic point for ammonium nitrate to be  $-17.35^\circ$ .<sup>4</sup> All attempts to determine the freezing-point of supersaturated solutions failed.

The decrease of  $\frac{\Delta}{m}$  and  $\frac{\Delta}{m'}$  is continuous from the most dilute to the most concentrated solutions. But from  $m = 4.7$  to 6.1 the decrease in  $\frac{\Delta}{m}$  is very small.

The eutectic point is  $-18^\circ.15$ . The two solutions  $m = 5.69$  and  $m = 6.43$  are supersaturated at their freezing temperature. As may be seen from the table, there is evidently a minimum for  $\frac{\Delta}{m}$ , corresponding to  $m = 3$  or thereabouts. From  $m = 6$  to 8,  $\frac{\Delta}{m'}$  is constant within the limits of experimental error.

<sup>1</sup> Phys. Rev. 3, 279 (1896). (Cited by Jones.)

<sup>2</sup> loc. cit. 269.

<sup>3</sup> Ann. Chim. Phys. (4) 25, 544 (1872).

<sup>4</sup> Bull. Soc. vaud. Sci. nat. 11, 27 (1872).

Sodium nitrate,  $\text{NaNO}_3$ , (85.09)

$m$	$m'$	$\Delta$	Loomis <sup>1</sup>	$\frac{\Delta}{m}$	de Coppet <sup>3</sup>	$\frac{\Delta}{m'}$
				Jones <sup>2</sup>		de Coppet
0.05	—	—	3.440	—	—	—
0.10	—	—	3.428	—	—	—
0.20	—	—	3.345	—	—	—
1.00	—	3.198	—	3.198	—	—
1.35	1.41	4.25	—	—	3.15	3.01
1.50	—	4.669	—	3.113	—	—
2.00	—	6.147	—	3.074	—	—
2.18	2.35	6.70	—	—	3.08	2.85
2.50	—	7.468	—	2.987	—	—
3.00	—	8.909	—	2.969	—	—
3.16	3.53	9.70	—	—	3.07	2.75
4.07	4.70	12.7	—	—	3.12	2.70
4.89	5.88	15.5	—	—	3.17	2.64
5.69	7.05	18.7*	—	—	3.29	2.65
6.43	8.22	21.7*	—	—	3.37	2.64

Ammonium sulphate,  $(\text{NH}_4)_2\text{SO}_4$ , (132)

$m$	$m'$	$\Delta$	$\frac{\Delta}{m}$	de Coppet <sup>5</sup>	$\frac{\Delta}{m'}$
			Jones <sup>4</sup>		de Coppet
0.05	—	0.024	4.80	—	—
0.10	—	0.469	4.69	—	—
0.20	—	0.818	4.09	—	—
0.50	—	0.969	3.94	—	—
0.72	0.76	2.80	—	3.88	3.65
1.00	—	3.686	3.69	—	—
1.38	1.52	5.45	—	3.75	3.58
1.40	—	5.133	3.67	—	—
1.98	2.28	8.20	—	4.14	3.59
2.52	3.04	11.1	—	4.40	3.65
3.01	3.79	14.4	—	4.78	3.77
3.24	4.17	16.2	—	5.00	3.88
3.46	4.56	18.0	—	5.20	3.94
3.66	4.92	20.4	—	5.57	4.14

<sup>1</sup> Phys. Rev. 3, 279 (1896). (Cited by Jones.)

<sup>2</sup> loc. cit.

<sup>3</sup> Ann. Chim. Phys. (4) 25, 544 (1872).

<sup>4</sup> loc. cit. 273.

<sup>5</sup> Ann. Chim. Phys. (4) 25, 536 (1872).

The eutectic point is  $-19^{\circ}.05$  according to my experiment. There appears to be a minimum both for  $\frac{\Delta}{m}$  and  $\frac{\Delta}{m'}$ .

Sodium sulphate,  $\text{Na}_2\text{SO}_4$ , (142.2)

$m$	$m'$	$\Delta$	Loomis <sup>1</sup>	$\frac{\Delta}{m}$	de Coppet <sup>3</sup>	$\frac{\Delta}{m'}$
				Jones <sup>2</sup>		de Coppet
0.05	—	—	4.590	—	—	—
0.10	—	—	4.340	—	—	—
0.14	0.14	0.60	—	—	4.29	4.29
0.20	—	—	4.071	—	—	—
0.28	0.28	1.20	—	—	4.29	4.29
0.30	—	—	3.875	—	—	—
0.35	0.35	1.425*	—	—	4.07	4.07
0.42	0.43	1.70*	—	—	4.05	3.95
0.50	—	1.839*	—	3.678	—	—
0.69	0.71	2.725*	—	—	3.94	3.84
0.84	0.86	3.05*	—	—	3.63	3.55
1.04	1.06	3.65*	—	—	3.51	3.44
1.36	1.41	4.50*	—	—	3.31	3.19

The eutectic point was found to be  $-1^{\circ}.2$  for the decahydrate  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , and  $-3^{\circ}.55$  for the heptahydrate  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ .<sup>4</sup> The solution  $m = 1.36$  is very highly supersaturated. It contains five times more anhydrous sodium sulphate than does the eutectic solution which freezes at  $-1^{\circ}.2$ .

There is no minimum. The decrease of both  $\frac{\Delta}{m}$  and  $\frac{\Delta}{m'}$  is continuous. The freezing temperatures observed by me are probably a little too low, and the progressive decrease of  $\frac{\Delta}{m}$  and  $\frac{\Delta}{m'}$  is probably still more marked than appears in the table. As the difficulty of getting a supersaturated solution to freeze without precipitation of salt increases with the quantity of solu-

<sup>1</sup> Phys. Rev. 3, 277 (1896). (Cited by Jones.)

<sup>2</sup> loc. cit. 274.

<sup>3</sup> Ann. Chim. Phys. (4) 25, 539 (1872).

<sup>4</sup> Bull. Soc. vaud. Sci. nat. 11, 33 (1872).

tion, only about 30 grams of solution were used for these experiments. As has already been stated, no correction was made for the increase in concentration due to the separation of ice.

My experiments in conjunction with those of Jones and others give evidence of the existence of a minimum for the salts enumerated in the first of the two following tables. In the second table are the salts for which, according to my experiments, there is no minimum, but a continuous decrease in the molecular-depression as the concentration increases. In both tables the values of  $\Delta$ ,  $\frac{\Delta}{m}$  and  $\frac{\Delta}{m'}$  are given for the most concentrated solution of each salt of which I was able to determine the freezing-point. The sign \* indicates that the solution is supersaturated at its freezing temperature.

Salts for which the molecular depression of the freezing-point presents a minimum

	$m$	$m'$	$\Delta$	Eutectic point	$\frac{\Delta}{m}$	$\frac{\Delta}{m'}$
Ammonium chloride, (NH <sub>4</sub> Cl)	3.27	3.74	13.7	-15°.8	4.19	3.66
Sodium chloride, (NaCl)	4.82	5.34	23.6*	-21.85	4.90	4.42
Barium chloride, (BaCl <sub>2</sub> )	1.13	1.23	7.5	-7.85	6.64	6.10
Magnesium sulphate, (MgSO <sub>4</sub> )	3.45	3.65	8.4*	—	2.44	2.30
Zinc sulphate, (ZnSO <sub>4</sub> )	2.64	2.74	10.1*	-6.55	3.83	3.69
Copper sulphate, (CuSO <sub>4</sub> )	1.88	2.00	3.9*	-1.6	2.08	1.95

Salts for which the molecular depression of the freezing-point decreases continuously as the concentration increases

	$m$	$m'$	$\Delta$	Eutectic point	$\frac{\Delta}{m}$	$\frac{\Delta}{m'}$
Strontium nitrate, (Sr(NO <sub>3</sub> ) <sub>2</sub> )	1.53	1.66	6.25*	-5°.75	4.09	3.77
Barium nitrate, (Ba(NO <sub>3</sub> ) <sub>2</sub> )	0.17	0.17	0.7	-0.7	4.12	4.12
Lead nitrate, (Pb(NO <sub>3</sub> ) <sub>2</sub> )	0.92	0.97	2.5	-2.7	2.72	2.58
Sodium carbonate, (Na <sub>2</sub> CO <sub>3</sub> )	0.75	0.75	2.8*	-2.1	3.73	3.33

It seems to be generally admitted that if  $n$  represents the number of molecules of the solute,  $N$  the number of molecules of the solvent, and  $\Delta$  the depression of the freezing-temperature of the solution, then

$$\Delta = \frac{n}{N} \times \text{const.}$$



Dissociation of the solute (electrolytic or hydrolytic) increases  $n$ ; and the formation of hydrates at the expense of the solvent decreases  $N$ . Both  $n$  and  $N$  are decreased by polymerization.

As these quantities vary, so the molecular-depression of the freezing-point increases, decreases or remains constant.

More than thirty years ago I showed that the continuous decrease in the molecular-depression of the freezing-point of an aqueous solution as the concentration of the solution increases, may be explained in two ways:

1. *By the dissociation of hydrates formed by the solute at the expense of the solvent.*<sup>1</sup>
2. *By dissociation of the solute,<sup>2</sup> probably hydrolytic dissociation.*<sup>3</sup>

I venture to recall this, now that the hydrate theory seems to be coming into favor again.

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<sup>1</sup> This theory was set forth at length in *Ann. Chim. Phys.* (4) 23, 377-386 (1871), and in *Bull. Soc. vaud. Sci. nat.* 10, 546-553 (1871). The fundamental assumptions were that the relative quantity of hydrate increases with dilution and with lowering of the temperature.

<sup>2</sup> *Ann. Chim. Phys.* (4) 25, 540 (1872).

<sup>3</sup> This was expressed in the following words: "La dissolution contient un mélange de combinaisons provenant de l'union d'une partie du dissolvant avec les produits de la décomposition du sel. Les proportions relatives du mélange varient avec la concentration et la température de la dissolution." *Bull. Soc. vaud. Sci. nat.* 11, 82 (1872).

# THE ELECTROLYSIS OF ACID SOLUTIONS OF ANILINE

BY LACHLAN GILCHRIST

When hydrochloric acid is electrolyzed, chlorine is set free at the anode, and it seemed quite feasible to dissolve a little aniline in the acid and let it be converted into chlor-aniline by the chlorine set free, just as the soda in the electrolysis of salt solutions is converted into hypochlorite.

Accordingly, a solution of 10 g of aniline, 50 cc of hydrochloric acid s. g. 1.2, and 50 cc water was made up, and a current of 30 amperes was passed through it, using pieces of platinum foil 2 x 5 cm as electrodes. It was not thought necessary to keep the aniline away from the cathode, as the chlor-aniline, once formed, is not easily reduced.

## Formation of aniline black

In a few minutes, however, a greenish smudge appeared at the anode and soon spread through the liquid. As this was obviously due to the formation of "aniline black" (one of the oxidation products of aniline) and meant an impure product and a bad yield, the experiment was broken off.

It is well known that in the electrolysis of hydrochloric acid oxygen is often given off together with the chlorine, the proportion depending on the concentration of the acid and on the current density. It therefore seemed possible that by reducing the latter and increasing the former the chlorine evolved might be more nearly pure, and the formation of the oxidation product prevented.

The attempt was made in the next electrolysis, in which  $\frac{1}{2}$  amp was passed through a solution of 5 g of freshly distilled aniline in 100 cc of hydrochloric acid of s. g. 1.2; but aniline black was formed as before. Four other experiments carried out under different conditions of current density and concentration gave the same result. In Experiment 6 a little mannite

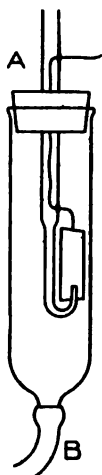
was added to the solution to prevent oxidation, but without effect.

TABLE I

No.	HCl s. g. 1,2	Aniline	Water	Current	Temp.
1	50 cc	10 g	50 cc	30 amp	18°-37°
2	100 cc	5 g	—	½ amp	18°-23°
3	100 cc	5 g	—	27 amp	30°-40°
4	100 cc	small amt	—	½ amp	25°
5	100 cc	small amt	—	1 ½ amp	24°-10° (in ice)
6	100 cc	10 g of HCl —aniline	10 cc	1 ½ amp	10° (in ice)

#### Determination of decomposition-voltage

The formation of aniline black in all these cases raised the question whether after all this substance might not be the primary product of the electrolysis; to test this point preparations were made to determine the decomposition-voltage of the solution.



The apparatus differed but slightly from that used by other investigators in measuring decomposition-voltages. The cathode cell is represented in Fig. 1, hydrogen was led in by A, and the connection with the anode compartment was effected through the narrow rubber tube B (25 cm long, 3 mm internal diameter.)

The first experiments were made with normal hydrochloric acid, and a good deal of trouble was experienced in obtaining accordant results. After a number of trials, however, it was found that:—

(i) Electrolytic hydrogen must be used in place of hydrogen from zinc and sulphuric acid.

(ii) The anode should be cleaned before each experiment, by treatment with hot nitric acid and water, then heated to red heat, then again washed with hot nitric acid, water, and alcohol, and dried in the air.

(iii) Changing the length of the anode wire from 2.5 mm to 1 mm has but little effect on the results.

(iv) Platinizing the anode wire has but little effect.

(v) Covering it with a glass tube, so as to reduce the volume of the anode compartment, has but little effect.

(vi) Shaking the anode has only a temporary effect ; but the solution must not mix with the cathode solution.

(vii) The measurements should be taken with rising E. M. F. If taken in the opposite direction the cell must be short-circuited between measurements, and then at least ten minutes must be allowed for the galvanometer to reach a steady state.

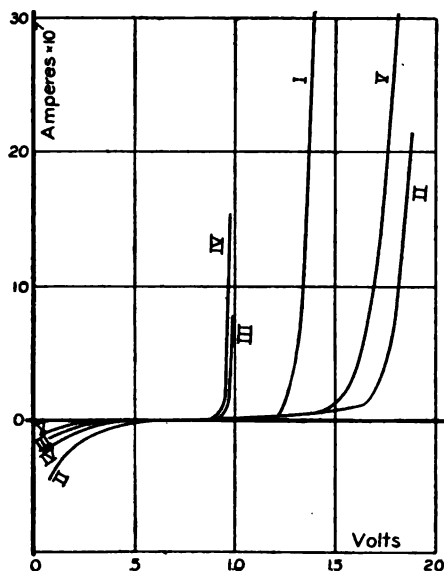


Fig. 2

If these points be attended to, fairly satisfactory measurements can be made; and the galvanometer comes to its final position within two to ten minutes from the time of changing the voltage.

The results of the work with hydrochloric acid are given in Table 2 and Curve I (Fig. 2). The curve rises suddenly at 1.25 volts; this is the well known "chlorine kink;" at lower voltages no chlorine is liberated from the solution. The result with

normal sulphuric acid is given in Table 3 and Curve II (page 541). The curve here rises suddenly at about 1.66 volts as is also well known.

TABLE 2  
Normal Hydrochloric Acid

Volts	Amperes $\times 10^7$	Volts	Amperes $\times 10^7$
1.18	-0.2	1.308	+6.3
1.213	+0.6	1.33	8.0
1.241	1.2	1.35	10.5
1.265	2.8	1.38	21.2
1.288	4.2	1.4	41.5

TABLE 3  
Normal Sulphuric Acid

Volts	Amperes $\times 10^7$	Volts	Amperes $\times 10^7$	Volts	Amperes $\times 10^7$
0.036	4.25	0.58	-0.08	1.208	+0.127
0.148	3.66	0.638	0.04	1.23	0.151
0.172	3.08	0.668	0.03	1.272	0.191
0.21	2.72	0.743	0.005	1.307	0.218
0.25	1.37	0.84	+0.028	1.334	0.28
0.319	0.87	0.876	0.043	1.46	0.41
0.36	0.69	0.943	0.058	1.493	0.98
0.421	0.61	1.005	0.07	1.659	1.18
0.484	0.38	1.139	0.093	1.786	6.12
0.546	0.27	1.176	0.109	1.875	21.2

Aniline hydrochloride was then dissolved in the normal hydrochloric acid in the proportion of one-tenth molecule per liter, and the measurements repeated. It was quite impossible to obtain a steady reading on the galvanometer, as the current kept falling for several hours after the voltage was applied (see Table 4). The same is true of solutions of aniline in normal sulphuric acid (see Table 5).

In these experiments of long duration the formation of aniline black at the anode could be observed ; that this was not due to oxidation by the air is shown by a blank experiment in which air was blown through the same solution in presence of a piece of platinum for 48 hours without causing the slightest turbidity or coloration.

TABLE 4  
Normal Hydrochloric Acid and Tenth-Normal Aniline

Volts	Amperes $\times 10^7$	Time
2	—0.042	4 min.
4	—0.018	6 "
4	—0.02	4 hrs.
6	+0.002	6 min.
6	—0.009	16 hrs.
6	—0.008	5 "
8	+0.03	6 min.
8	—0.002	3 hrs.

TABLE 5  
Normal Sulphuric Acid and Tenth-Normal Aniline

Volts	Amperes $\times 10^7$	Time
10	—0.34	4 min.
10	0.63	19 hrs.
15	0.12	4 "
19	0.62	10 min.
19	0.38	34 "
19	0.015	20 hrs.
22	2.72	50 min.
22	1.5	2 days
24	6.18	4 min.
24	3.67	1½ hrs.
24	3.3	½ hr.
27	10.0	7 min.

Dark greenish smudge commenced to form

27	11.3	7½ min.
27	13.2	8 "
27	19.2	1 hr.
27	22.3	1 "

The cell was again filled with the aniline acid solution, hydrogen passed in at the large electrodes as before, the primary circuit broken at Y, and the current and E. M. F. determined. Both rose steadily until the current reached  $1.4 \times 10^{-7}$  amp and the E. M. F.  $V = 0.012$  volt, after which the voltage fell, the current increased, and aniline black appeared in the anode solution.

From these experiments it is clear that a definite current for each voltage is not to be expected; the figures given in Table 6 and plotted in Curve III were therefore arbitrarily taken four minutes after adjusting the E. M. F. The sudden rise in the curve occurs at 0.95 volt, 0.30 volt below the chlorine kink. This shows that the aniline acts as a "depolarizer" in hydrochloric acid solution, but whether owing to the formation of a chlor-aniline, or of aniline black, does not appear.

TABLE 6  
Normal Hydrochloric Acid and Tenth-Normal Aniline

Volts	Amperes $\times 10^7$	Volts	Amperes $\times 10^7$	Volts	Amperes $\times 10^7$
0.029	-1.7	0.432	-0.01	0.739	+0.01
0.099	1.33	0.472	0.002	0.784	0.01
0.19	0.54	0.485	0.000	0.84	0.014
0.264	0.21	0.535	+0.004	0.91	0.055
0.328	0.08	0.569	0.006	0.936	0.2
0.368	0.05	0.609	0.006	0.971	1.37
0.403	0.02	0.664	0.007	0.988	4.3

#### Decomposition voltages in sulphuric acid solutions

A set of measurements was then made under the same conditions as those of Table 4, but using normal sulphuric acid and one-tenth mol of aniline sulphate per liter, instead of the hydrochloric acid and the chloride. The results are contained in Table 7 and Curve IV.

Curve IV has its kink at the same voltage (0.95 volt) as Curve III for the experiments in which hydrochloric acid was used. The simplest explanation is that in both cases the same product is formed; in absence of hydrochloric acid this can not

be chlor-aniline; it must therefore be an oxidation product, presumably the aniline black.

With this difference of 0.30 volt in favor of the oxidation, it seems very unlikely that any chlorine could be liberated in hydrochloric acid to which aniline had been added. By increasing the current density at the anode sufficiently, however, it might be possible to oxidize the aniline at that electrode more quickly than it could be replaced by convection or diffusion; so that, for part of the time, the solution would consist of pure hydrochloric acid, and chlorine would be liberated. At best the yield of chlor-anilines would be low, and the product impure.

TABLE 7  
Normal Sulphuric Acid and Tenth-Normal Aniline

Volts	Amperes $\times 10^1$	Volts	Amperes $\times 10^1$
0.029	-2.7	0.667	-0.015
0.111	1.48	0.711	0.002
0.21	1.06	0.742	+0.002
0.273	0.75	0.778	0.008
0.341	0.5	0.814	0.012
0.374	0.347	0.847	0.02
0.406	0.25	0.872	0.042
0.438	0.19	0.909	0.145
0.479	0.132	0.941	0.8
0.506	0.125	0.956	2.5
0.538	0.072	0.969	7.45
0.577	0.039	0.948	15.5
0.604	0.023	Aniline black commenced to form before last reading was made	

These conclusions are in agreement with the results of an experiment in which 100 grams of aniline were dissolved in 450 cc of hydrochloric acid of s. g. 1.2, and electrolyzed with a current of 7.5 amperes for  $7\frac{3}{4}$  hours. The anode was a piece of arc light carbon 11 cm long; the cathode platinum 2 x 5 cm. No chlorine was noticed in the gases given off. The vessel containing the electrolyte was surrounded by an ice-bath, but the temperature rose to 38° C.

After the electrolysis the dark liquid was filtered and



evaporated. On cooling, 50 grams of crystals were deposited, and three days later another crop of fourteen grams was obtained. These crystals, and the final mother-liquor were examined for chlor-aniline by adding caustic soda in excess, extracting with ether, removing the ether on a water-bath, and fractionating the residual oil. The boiling-point rose rapidly to  $179^{\circ}$ , and all but 4 or 5 cc passed over at  $179^{\circ}$ – $181^{\circ}$ , the boiling-point of aniline. The residue contained a little chlorine; thus while chlor-anilines are formed, they amount to but a few percent of the weight of the aniline employed.

#### Aniline and hydrobromic acid

As the oxidation potential of aniline (0.95 volt) lies above the decomposition voltage of hydrobromic acid (0.75 volt in 4-*n* HBr), it follows that on electrolysis of a solution of aniline in hydrobromic acid bromine will be liberated, and aniline black will not be formed. This conclusion is confirmed by the following experiment.

25 g of potassium bromide, 12.5 cc of pure sulphuric acid, and 0.9 g of aniline were dissolved in water, the total volume of the solution being 65 cc; a precipitate of potassium sulphate was removed by decantation.

TABLE 8  
*n*-Sulphuric Acid, *n*/10 *m*-Nitriline

Volts	Amperes $\times 10^7$	Volts	Amperes $\times 10^7$
0.20	—1.20	1.56	+3.3
0.21	0.27	1.59	4.0
0.27	0.17	1.62	6.8
0.31	0.11	1.65	9.0
0.41	0.02	1.69	12.0
0.75	+0.08	1.73	15.32
0.96	0.22	1.75	18.1
1.27	0.30	1.76	20.4
1.47	0.78	1.79	26.0
1.53	1.82	1.81	29.0

A current of 0.25 ampere was passed through this solution between platinum electrodes (anode 2 x 5 cm, cathode 2 x 1 cm)

for ten minutes. No aniline black was formed, but the anode became covered with a deposit of white matted crystals, stained with bromine. These crystals were removed, washed, and dried and their melting-point found to be  $116^{\circ}$ ; *s*-tribrom-aniline melts at  $118^{\circ}$ .

#### *m*-Nitr-aniline

From chemical considerations it seemed probable that nitr-aniline would be less easily oxidized than aniline itself. To test this view, a series of experiments analogous to those of Curve IV were undertaken, in which *m*-nitr-aniline, instead of aniline was dissolved in the sulphuric acid.

The results are plotted in Curve V. The oxidation potential of *m*-nitr-aniline lies at 1.43 volts, 0.2 above the chlorine kink.

#### Summary

The conditions under which decomposition-voltages can be determined in acid solutions of aniline are specified (page 541).

The formation of aniline black from *n*/10 aniline in solutions of *n*-hydrochloric acid or *n*-sulphuric acid takes place at 0.95 volt (small anode, hydrogen cathode).

Therefore only traces of chlor-aniline are formed on electrolysis of aniline in hydrochloric acid solution; but brom-anilines are formed by the electrolysis of solutions containing hydrobromic acid and aniline. The aniline solutions thus resemble those of phenol.<sup>1</sup>

The oxidation potential of *m*-nitr-aniline in sulphuric acid solution (1.43 volts), is much higher than that of aniline.

My thanks are due to Prof. W. Lash Miller, at whose suggestion these measurements were carried out.

*University of Toronto,  
June, 1904*

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<sup>1</sup> Zehrlant. Zeit. f. Elektrochem. 7, 501 (1901).

# AN ANALYTICAL STUDY ON THE DEPOSITION OF ALUMINUM FROM ETHYL BROMIDE SOLUTION

BY HARRISON EASTMAN PATTEN

## Introduction

In 1902 W. A. Plotnikoff made the interesting discovery that aluminum bromide dissolved in ethyl bromide yields a solution of exceptionally good conductivity.<sup>1</sup> He deposited crystalline aluminum from this solution upon a carbon electrode, but gave no conditions save the exclusion of moisture. As numerous attempts at depositing aluminum have failed or only partially succeeded, I have studied the electrolysis of this solution.

The factors to be considered are : temperature ; concentration ; anode and cathode potentials ; electrode materials ; conductivity of solution ; current density ; film formation or passive state of aluminum ; and the physical state of the deposit.

For convenience and clearness, the experimental work is presented under two divisions : (1) Total decomposition curves for a moderately concentrated solution ; (a) with polished platinum electrodes, (b) with platinized platinum electrodes, both showing no aluminum deposited ; (c) with aluminum electrodes, and (d) a curve showing the fall of potential of aluminum against platinum with time, which accounts for the non-corrosion of the aluminum anode observed in (c). (2) Anode, cathode, and total decomposition curves for platinum electrodes, in a concentrated solution from which aluminum was deposited at low current density.

## Experimental

### I.

Aluminum bromide, prepared by passing bromine vapor over heated aluminum in a current of carbon dioxide, was dissolved in anhydrous ethyl bromide. This solution showed a

<sup>1</sup> Jour. Russ. Phys. Chem. Soc. (3) 466 (1902).

specific gravity of 1.405 at 20° C, as compared with water at 4° C. 7.586 grams of solution at this temperature gave 0.0635 g  $\text{Al}_2\text{O}_3$ , which corresponds to 0.3324 g  $\text{AlBr}_3$ , a percent of 4.38 upon the total weight of solution. One gram-molecule of  $\text{AlBr}_3$  is contained in 4.34 liters, or one gram-equivalent in 1.43 liters. At 20.5° C the specific conductivity was  $3.763 \times 10^{-4}$  reciprocal ohms (Kohlrausch method).

This solution was electrolyzed between platinized electrodes in a dry cell<sup>1</sup> at 15° C, the temperature being controlled by a water-bath. The method used to measure the impressed voltage and the corresponding current through the cell is given in a former paper.<sup>2</sup> In Table Ia the electromotive force was read by compensation, and the current calculated by taking the drop in voltage across a known resistance placed in series with the cell; in Table Ib a voltmeter was used and the current measured by a Weston milliammeter.

Table Ia shows a well defined CR line for low current densities, and a polarization value of 0.6 volt at about 0.0001 ampere per square centimeter. Bromine is liberated at the anode. (A plate of aluminum after being allowed to coat itself by standing in the air gives 0.632 volt in this solution against a platinum cathode.)

Table Ib shows that a solution of this low concentration does not yield metallic aluminum even at comparatively high current densities. The discharge potentials confirm this: 0.069 volt was obtained from a current density of 0.007 ampere per sq. cm., and 0.263 volt from 0.033 ampere per sq. cm., whereas deposited aluminum has a total discharge potential against platinum of 2.3 volts (in this solution) and a single potential of 1.1 volt again aluminum bromide in ethyl bromide, as will be shown below. The time which elapsed between the release of

<sup>1</sup> For dimensions of cell see "Single Potentials of Zinc, Etc." Patten and Mott. Trans. Am. Electrochem. Soc. 1903, Vol. III.

<sup>2</sup> "Decomposition Curves of Lithium Chloride in Various Alcohols and the Electrodeposition of Lithium." Patten and Mott. Jour. Phys. Chem. March, 1904.

the impressed E. M. F. and the taking of the discharge potential was near one-tenth of a second.

TABLE Ia.

AlBr<sub>3</sub> in C<sub>2</sub>H<sub>5</sub>Br.

4.38 percent.

 $t = 15^{\circ} \text{ C.}$ 

Volts	Amperes	Amperes per sq. cm.
0.282	0.000072	0.000024
0.535	0.000142	0.000047
0.791	0.000769	0.000256
0.930	0.00108	0.00036
1.301	0.00228	0.00076
1.408	0.00265	0.00088
1.681	0.00345	0.00115

TABLE Ib.

 $t = 15^{\circ} \text{ C.}$ 

Volts	Amperes	Amperes per sq. cm.
1.0	0.0015	0.0005
1.5	0.0025	0.0008
2.0	0.0044	0.0014
2.5	0.0065	0.0021
3.0	0.0075	0.0025
3.5	0.010	0.0033
4.0	0.012	0.004
4.5	0.013	0.0043
5.0	0.015	0.005
5.5	0.016	0.0053
6.0	0.018	0.006
7.0	0.021	0.007
8.0	0.023	0.0076
9.0	0.026	0.0086
10.0	0.028	0.0093
15.0	0.036	0.012
20.0	0.046	0.015
25.0	0.060	0.020
30.0	0.067	0.022
40.0	0.077	0.025
50.0	0.093	0.031
99.0	0.139	0.046

To ascertain the effect of surface condition of the platinum cathode upon the deposition of aluminum from this solution a

second portion of this same solution was electrolyzed between polished platinum electrodes. Table IIa was taken by the potentiometer method used for Table Ia and there cited.

TABLE IIa.

AlBr<sub>3</sub> in C<sub>2</sub>H<sub>5</sub>Br.

4.38 percent.

$t = 15^{\circ} \text{C.}$

Volts	Amperes	Amperes per sq. cm.
0.90	0.000238	0.000158
1.60	0.000452	0.000301
1.99	0.000602	0.000401
2.90	0.00101	0.000674
3.84	0.00156	0.00104
4.80	0.00199	0.001326
5.76	0.00241	0.001605
6.70	0.00306	0.00204
8.60	0.00405	0.0027
11.44	0.00562	0.0037

TABLE IIb.

- Volts	Amperes	Amperes per sq. cm.
10.0	0.005	0.00333
15.0	0.0075	0.005
20.0	0.0095	0.0063
25.0	0.012	0.0080
30.0	0.014	0.0094
35.0	0.0166	0.0110
40.0	0.0185	0.0123
45.0	0.0208	0.0139
50.0	0.0226	0.0150
55.0	0.0245	0.0163
60.0	0.026	0.0173
70.0	0.0305	0.0203
80.0	0.034	0.0226
90.0	0.038	0.0253

The curve obtained from Table IIa shows a polarization of 0.7 volt, comparable with the value given by Table Ia for platinized electrodes. Table IIb shows that with increasing current density metallic aluminum does not deposit from a solution of this concentration. A discharge from 0.013 ampere per

sq. cm. gave 0.356 volt. Evidently the surface condition of the platinum is a minor factor in depositing aluminum.

In the same solution a current — E. M. F. curve was taken at 18° C, using aluminum electrodes. The readings are given in Table III, and the curve drawn from them indicates a polarization of 0.8 volt for a current density near 0.00025 ampere per sq. cm. If the aluminum anode were smoothly attacked and aluminum deposited at the cathode there would be no polarization. These aluminum electrodes give approximately the same value as that for platinum electrodes.

TABLE III.  
Aluminum Electrodes.  $\text{AlBr}_3$  in  $\text{C}_2\text{H}_5\text{Br}$ . 4.38 percent.

Volts	Amperes	Amperes per sq. cm.
2.0	0.0006	0.00015
3.0	0.001	0.00025
5.0	0.002	0.0005
7.0	0.003	0.00075
8.0	0.0035	0.00087
9.0	0.0040	0.0010

As a check the potential of aluminum was determined in this solution against a platinum cathode at 15° C. This gave 0.632 volt. This low value, corresponding so closely to the polarization values given by Tables Ia, IIa and III, suggest that we have to do with a coating on the aluminum. To investigate this a current of 0.010 ampere — approximately 0.5 ampere per sq. cm. — was passed between a platinum cathode and an aluminum anode for several minutes, and the discharge taken. This gave the same low value recorded above. However, on reversing the current and using the aluminum as cathode while electrolyzing, the discharge potential for the total cell was 2.235 volts.<sup>1</sup> Readings taken at intervals after releasing the impressed E. M. F are given in Table V.

<sup>1</sup> Using Poggendorff's compensation method with a d'Arsonval galvanometer sensitive to one-half megohm.

These values are plotted in Plate I with volts as ordinates and minutes as abscissas. The rapid decrease of discharge pressure with time points strongly to the formation of a film<sup>1,2,3</sup> upon

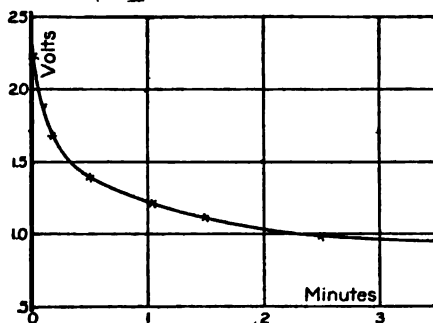


Plate I.

Al — Pt in  $\text{AlBr}_3 + \text{C}_2\text{H}_5\text{Br}$ 

4.38 percent

 $t = 15^\circ$ 

TABLE V.

Discharge Potential. Aluminum-Platinum.  $\text{AlBr}_3$  in  $\text{C}_2\text{H}_5\text{Br}$ .  
4.38 percent.  $t = 15^\circ \text{C}$ .

Minutes	Seconds	Volts
0	0	2.235
0	10	1.675
0	30	1.395
1	30	1.117
2	30	0.980
3	30	0.952

the aluminum. With the exception of an aqueous solution of ammonium chloride, this film has been observed hitherto in solutions of oxygen acids or their salts; and if we consider the

<sup>1</sup> "The Alloying of Metals as a Factor in Electroplating." L. Kahlenberg. *Electrochemical Industry*, 1, 6, 201 (1903).

<sup>2</sup> "The Physical Characteristics of Metal Deposits." *Ibid.* 1, 6, 204 (1903).

<sup>3</sup> "The Corrosion of Aluminum and Its Prevention." W. R. Mott. *Ibid.* 11, 4, 129 (1904).



water, as we should, in that case also we have oxygen. Here the only oxygen present is a minute trace due to action of the moisture in the air upon the constituents of the solution during a transfer which was well nigh unavoidable; and below it is shown that this trace is insufficient to induce the formation of a film. Consequently we have a case where aluminum forms a protective coating in a solution containing a halogen radical, and in which the halogen salt of aluminum is soluble to a marked degree.

## II.

A fresh sample of aluminum bromide was prepared by passing bromine over aluminum turnings in a hard glass tube heated to redness. The crude product was redistilled, the first few fractions rejected, and the final runnings<sup>1</sup> dissolved in ethyl bromide, which was also my own preparation, dried over fused calcium chloride and distilled. At 20° C the solution had a specific gravity of 1.671, and analysis gave 0.799 gram of  $\text{Al}_2\text{O}_3$  in 10.214 grams of solution, the equivalent of 4.183 grams of  $\text{AlBr}_3$ , giving 40.95 percent of  $\text{AlBr}_3$  by weight upon the total weight of solution. This corresponds to one gram-molecule in 0.391 liter, or one gram-equivalent in 0.127 liter.

The solution was electrolyzed in a cell made of a small wide-mouth bottle (A, Fig. 1), through whose stopper passed two glass tubes (I and J) with polished platinum electrodes each one-half square centimeter in area fused in their lower ends. A third perforation in the stopper permitted a U-tube (B) packed with ignited asbestos wick to dip into the solution. The outer end of this U-tube was led through a stopper into a second portion of this same solution ( $\text{AlBr}_3$  in ethyl bromide) contained in the short test-tube, C. A second U-tube filled with ignited asbestos fiber (D) connected this second aluminum bromide solu-

<sup>1</sup> On allowing the liquid aluminum bromide to solidify, crystals were formed. Some of these had planes nearly one-fourth square centimeter in area; they belong in the rhombohedral division of the hexagonal system, and resemble calcite. The purified aluminum bromide is not white, but a very light yellow.

tion with a solution of aluminum bromide in absolute ethyl alcohol contained in the test-tube, E; and a third asbestos filled tube (F) gave contact between this alcohol solution and the small beaker (G) containing 0.1 normal aqueous potassium chloride into which the siphon (L) of an Ostwald half cell (H) dipped. With the exception of the potassium chloride, all solutions were protected from the air by tightly-fitting stoppers of pure rubber and the two protection vessels effectually prevented diffusion of water into the electrolytic cell, while they also afforded electrical connection between the electrodes in the cell (A) and the Ostwald electrode (H).

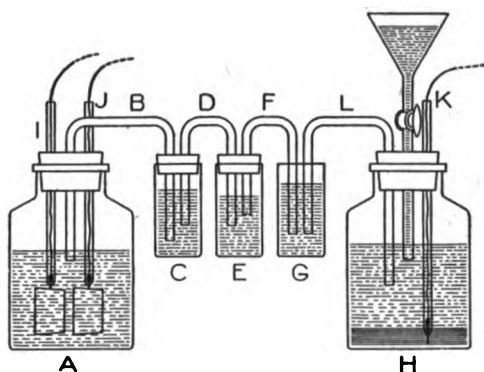


Fig. 1

Having thus constituted the system, pressure from a storage battery, regulated by a water rheostat, was applied to the cell through mercury contact in the tubes I and J and the voltage drop across (1) the total cell, (2) anode to Ostwald cell and (3) cathode to Ostwald cell taken on a potentiometer, using Poggendorff's method, while the current passing through the cell was also read. This current when small was gotten by taking the voltage—by compensation—across a known resistance placed in series with the cell, and calculating current from Ohm's law. The electrical connections were similar to those given in full in a previous paper.<sup>1</sup> Two zero instruments were used; one a

<sup>1</sup> "Decomposition Curves of Lithium Chloride in Various Alcohols, Etc." Patten and Mott. Jour. Phys. Chem. March, 1904.

portable d'Arsonval, sensitive to one-half megohm; the other a mirror form of d'Arsonval with a figure of merit near  $2.00 \times 10^{-8}$ . For readings on the total E. M. F. across the cell, and for determining the voltage used to calculate the current passing through the cell, the portable instrument served every purpose, but the resistance of the intermediate vessels B, C, D, E, F, G, L, H, used to get the anode and cathode voltage drop, was so great that the portable galvanometer gave only a very coarse adjustment. The mirror galvanometer was then used to get the accurate setting. The electrodes were heated to redness before use.

The readings are given in Table VI. Column I contains the total E. M. F. impressed upon the cell; column II, the voltage drop across anode to half-cell, correction being made for the  $-0.56$  volt of the latter; column III, the cathode to half-cell voltage drop, also corrected for the  $-0.56$  volt; column IV, the current density in amperes per square centimeter corresponding to the impressed E. M. F. given in column I; and column V, the current in amperes from which column IV is calculated.

TABLE VI.  
Aluminum Bromide in Ethyl Bromide  
40.95 percent.  $t = 20^{\circ} \text{C.}$

Volts			Amperes	
I. Total	II. Anode	III. Cathode	IV. Current density	V. Current
0.3007	—	0.790	0.0000270	0.0000135
0.785	—1.050	—0.364	0.0000890	0.0000445
1.024	—1.230	—0.160	0.000298	0.000149
1.441	—1.295	+0.217	0.001072	0.000536
1.850	—1.434	+0.365	0.00230	0.00115
2.350	—1.310	+1.018	0.001386	0.000693
2.400	—1.333	+1.031	0.00144	0.000720
2.578	—1.440	+1.116	0.00240	0.00120
2.852	—1.598	+1.166	0.00504	0.00252
3.16	—1.773	+1.321	0.00680	0.00340
3.50	—2.040	+1.531	0.01016	0.00508
4.23	—2.387	+1.701	0.01548	0.00774
7.37	—5.25	—	0.042	0.021
9.70	—	+4.10	0.058	0.029
Discharge	—0.81	+0.81		

Table VI is graphically represented in Plate II. Ordinates are in amperes per square centimeter of electrode surface.<sup>1</sup> The curve "Total" was gotten from column I and column IV, and shows the variation of current density with increasing E. M. F. Since the two platinum electrodes dipping into the solution op-

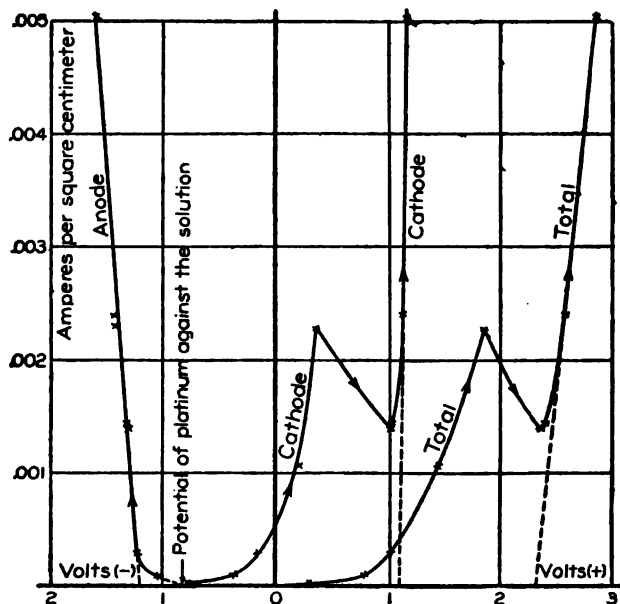


Plate II.  
 $\text{AlBr}_3$  dissolved in  $\text{C}_2\text{H}_5\text{Br}$   
 40.95 percent  
 Platinum electrodes  
 $t = 20^\circ \text{C.}$

pose each other, with zero impressed E. M. F. the cell shows no polarization, and the curve rises from the zero point of the chart. The current density increases rapidly with the E. M. F. until a value 0.0023 ampere per sq. cm. is reached. Near this point aluminum is deposited faster than the solution can redissolve it, its counter E. M. F. is exerted, and in consequence the current density falls off until the impressed E. M. F. rises beyond 2.3

<sup>1</sup> In this case the anode and cathode were both of the same area.

volts when the curve becomes the straight CR line of the conducting solution.

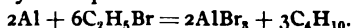
The curve "Cathode" is plotted from columns III and IV. It rises, not from zero, but from the value of platinum against the solution,  $-0.8$  volt.<sup>1</sup> The similarity between curves "Total" and "Cathode" is apparent at a glance, and is due to the fact that the reaction at the cathode is manifest in the total curve for the cell.

The "Anode" curve also rises from  $-0.8$  volt, as would be expected, but since only one pronounced reaction—the liberation of bromine—occurs, the curve becomes a CR line after reaching the current density  $0.00015$  ampere, at which sufficient bromine is deposited to give the polarization  $-1.20$  volt, its single potential against the solution.

Producing the CR lines of these three curves to the axis of volts gives a single potential for aluminum of  $+1.1$  volts; for bromine,  $-1.2$  volts; and a polarization of  $+2.3$  volts for the cell as a whole. The agreement of this value with the instantaneous discharge potential given in Table V and Plate I is excellent, and of course to be expected. The rapid decrease in the discharge potential with time indicates, too, why the single discharge potentials for anode and cathode given in Table VI are lower than those gotten by extending back their respective CR lines in Plate II.

Aluminum was deposited in crystals treeing out from the edges of the cathode. The metal reacts upon the solution vigorously, giving off a gas—probably largely  $C_4H_{10}$ . It has been shown that aluminum coated by standing in the air is not readily

<sup>1</sup> Compare with the value  $-0.83$  volt for platinum against lithium chloride in water (Jour. Phys. Chem. March, 1904, pages 162 and 163). This single potential is usually attributed to oxygen in the platinum. If that be assumed here as true, we have a partial explanation of the formation of a film and the failure to deposit aluminum from dilute solutions of aluminum bromide in ethyl bromide. Still, having this apparent oxygen potential also in concentrated solution, we have no indication of a film; the aluminum deposits in a regular manner and is redissolved because of its action upon the ethyl bromide as partially expressed by the equation:



acted upon by this solution. The voltages, of course, vary correspondingly. This is considered more fully under the head "Aluminum as Anode."

By quickly shifting the electrodes from the solution to 95 percent ethyl alcohol scales of aluminum were removed from the cathode. The metal is coated with a film and dull. It does not adhere to the platinum, but strips readily. Hydrochloric acid dissolved the metal with evolution of hydrogen.

At the anode bromine is liberated and diffuses rapidly, thus rendering difficult the deposition of aluminum in quantity without a diaphragm. The platinum electrode showed no sign of corrosion.

#### **Aluminum as anode**

Isenburg<sup>1</sup> got 60 to 47 volts counter pressure from an aluminum anode. This he most reasonably explained as a condenser effect caused by the high resistance film upon the anode. S. R. Cook,<sup>2</sup> repeating the work of Isenburg, which he seems to have overlooked, attributes this action of the aluminum anode in aqueous solutions of oxy-salts and acids to an accumulation of ions which set up a higher counter E. M. F. by reason of their inability to discharge through this high resistance film. He gives 17.5 volts counter pressure from 26 volts applied during one hour, seven minutes and thirty seconds. In that time the current fell off from 9.000 amperes to 0.070 ampere. Air bubbled over the anode caused the current to rise to 0.35 ampere; when the air current was interrupted the current fell again to 0.07 ampere. The solute used was potassium aluminum sulphate.

The distinction between Isenburg's explanation and that of Cook is not deep seated. Both require the film. The solution in contact with the film may be constituted of small particles of atomic magnitude, or it may not; likewise the film. This whole situation may be expressed thus: when used as anode in certain solutions aluminum becomes coated with a protective

<sup>1</sup> Zeit. f. Elektrochemie, 9, 278-280 (1903).

<sup>2</sup> Physical Review, 18, 23 (1904).

film<sup>1</sup> of high resistance which hinders the passage of the current. The observed condenser action is only what is to be expected, having two conductors separated by a dielectric. The breaking down of the film under high voltage and the effect of temperature upon this "critical" voltage are normal phenomena, easily comprehended aside from assumptions. F. Fischer<sup>2</sup> has shown the effect of temperature upon this penetration of the film; and its breakdown is seen to be merely a question of concentrating enough energy upon it to force a passage, or to secure a temperature sufficient to cause its solution in the electrolyte. It is doubtful if even a true electrolytic capacity<sup>3</sup> gains vividness by expression in terms of the ionization theory, inasmuch as it is due to the products of electrolysis discharging out of phase with the current which deposited them; and we need not assume ionization in order to treat the effect upon the wave form mathematically. In the case of the high discharge of Isenburg we have certainly a charge upon the solution, and another upon the aluminum anode; but it by no means follows that in the solution this charge resides upon ions. Experimental data upon ionic migration shows a change in concentration of the solute *as a whole*. There is nothing in the work of Isenburg or of Cook or of Fischer which necessitates the assumption that uncombined electrically charged negative radicles are massed about the anode. The more light we have upon the behavior of aluminum, the closer we come to a purely material problem;

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<sup>1</sup> Compare with the high resistance films upon the cathode obtained by electrolyzing lithium chloride in various solvents. This cathode resistance film gave no such high discharge pressure as Isenburg and Cook report for the anode film. If the phenomenon be due to a massing of undischarged ions about the electrode it is to be expected that cations show counter E. M. F. under comparable conditions. The time between release of applied E. M. F. and reading of counter E. M. F. was near one-tenth of a second. It is possible that a shorter time interval would show this condenser effect for the cathode film. These observations are given in a former paper, "Decomposition Curves of Lithium Chloride in Alcohols, Etc. (Jour. Phys. Chem. 8, 153 (1904)) and in a series of abstracts to be found in the *Electrochemical Industry*, 1, 12, August, 1903.

<sup>2</sup> F. Fischer. *Zeit. Phys. Chem.* 48, 177 (1904).

<sup>3</sup> F. Krüger. *Ibid.* 45, 1 (1903).

when the conditions requisite for removing the films are met, the metal behaves normally; and these conditions are no more peculiar than for other chemical processes.

The solution of aluminum bromide used in my experiments was free from oxygen in a high degree. And yet a number of points indicate that a film is formed, that we get the anode action of aluminum, and no high discharge pressure:—

(1) Using anode and cathode of aluminum a polarization of 0.8 volt was obtained. Consult Table III.

(2) An aluminum anode against a platinum cathode gave 0.7 volt, even after electrolyzing several minutes; and the current decreased with time.

(3) After a current had been passed for several minutes while the aluminum served as cathode, the same sheet of aluminum used in (2) gave 2.235 volts against platinum. See Plate I, Table V.

(4) The decomposition curves obtained with platinum electrodes show a low polarization value—about 0.8 volt—for rather high current densities; and the discharge potentials are considerably lower, though read within one-tenth of a second after releasing the impressed E. M. F.

(5) The discharge potential 2.235 volts cited in (3) falls off with time—as shown in Table V and Plate I—till a value comparable with those given in (1), (2), and (4) is reached.

(6) The decomposition value of 2.30 volts—obtained graphically in Plate II, "Total" curve from data given in Table VI—agrees with the discharge potential given in (5), as well as with the sum of the anode and cathode polarization from Plate II.

(7) Aluminum was obtained and removed from the solution which gave this value, 2.30 volts.

(8) Other metals also show a potential lower than is to be expected in this solution (4.38 percent). At 18° C magnesium gave a value of 0.797 volt, which rose to 0.838 volt; copper, 0.790 volt; lead, 1.014 volts; cadmium, 0.846 volt; and zinc, 0.795 volt. These readings are taken against the same platinum



cathode in each case, and are for the total cell. Platinum itself has a single potential of near  $-0.80$  volt against this solution, as will be seen from Plate II. The effect of a film in decreasing effective voltage is evident.

Table VII gives the influence of change in concentration upon the E. M. F. for magnesium, manganese and aluminum against platinum. Under each metal is given the total E. M. F. for the cell, and at the left is the corresponding percentage composition of the solution by weight. The measurements were made by compensation, using the portable galvanometer previously described.

TABLE VII.  
Potential of Metals Against Platinum in  $\text{AlBr}_3 + \text{C}_2\text{H}_5\text{Br}$

Percent $\text{AlBr}_3$	Volts		
	Magnesium	Manganese	Aluminum
49.4 <sup>1</sup>	1.636	0.767	0.984
26.8	2.277 <sup>1</sup>	0.943	0.985 <sup>2</sup>
18.4	2.015	0.757	—
14.0	1.955	—	—
11.0	1.935	—	—
9.5	1.920	—	—
8.2	1.920	—	—

Taking the single potential of bromine against the solution as  $-1.20$  volts from Plate II, the single potential of magnesium against a 26.8 percent solution of aluminum bromide in ethyl bromide is  $+1.077$  volts. Here again manganese and aluminum give low values indicative of film formation. The low voltage 1.575, given by magnesium in the 26.8 percent solution, is due to the formation of magnesium bromide which is not dissolved away quickly. As soon as this coat is gone we get the higher value, 2.277. Conversely, by allowing the magnesium

<sup>1</sup> In the 26.8 percent solutions the instantaneous value for magnesium was 1.575 volts, rising quickly to 2.277 volts, the value in the table.

<sup>2</sup> This value rapidly fell to  $+0.582$  volt.

to dissolve until the solution became rich in magnesium bromide the E. M. F. fell to 1.500 volts.

The decrease in voltage with increasing dilution is contrary to the needs of Nernst's theory. On the other hand, it seems that we have the voltage passing through a maximum at or near 27 percent of  $\text{AlBr}_3$  in ethyl bromide. Now Plotnikoff<sup>1</sup> has shown that the molecular conductivity of  $\text{AlBr}_3$  in this solvent falls rapidly and then slowly rises with increasing dilution. While of course the conductivity cannot influence difference of potential gotten by a zero method, still it indicates a change in the nature of the solution which appears to go hand in hand with this maximum E. M. F. of magnesium. Reference to Plotnikoff's concentration curve shows a rapid change in molecular conductivity at these dilutions, and this I have confirmed experimentally. In this connection the point should be made that the dielectric constant of ethyl bromide is only 8.90. This is an excellent illustration of the failure of the Nernst-Thomson rule, for the above solutions conduct well. The combination of solvent and solute to form a new compound can hardly be urged in extenuation, since such union is now very generally conceded in all cases of solution.

Recurring to the work of Cook,<sup>2</sup> it seems from the experimental data set forth above, that his theory of a counter E. M. F. produced by a layer of ions at the anode is not applicable in this solution. However it is not impossible that at lower concentration of  $\text{AlBr}_3$  a film of sufficient resistance might be formed upon an aluminum anode to afford this high counter pressure. And it would be desirable to test this, as well as to take the discharge within a shorter time interval.

The use of a fused nitrate<sup>3</sup> with aluminum anode and iron cathode shows that even at fairly high temperature aluminum

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<sup>1</sup> l. c.

<sup>2</sup> Burgess and Hambuechen. *Trans. Am. Electrochem. Soc.* 1, 147 (1902); *Electrochem. Industry*, 1, 6, 204 (1903). Cf. W. R. Mott. *Ibid*, 2, 4, 129 (1904); also 2, 7, 268 (1904); also C. I. Zimmerman. *Trans. Am. Electrochem. Soc.* 5, 147 (1904).

exerts its rectifying action upon an alternating current. This indicates that the film formation is not solely a question of temperature.

### Conclusions

(1) It has been shown that Plotnikoff's values for the conductivity of aluminum bromide dissolved in ethyl bromide are reliable; and his deposition of crystalline aluminum from such a solution has been confirmed.

(2) Crystals of aluminum bromide near 0.5 centimeter on edge were formed from the fused salt. They belong in the rhombohedral division of the hexagonal system, and resemble calcite. The purified aluminum bromide is not white, but a very light yellow.

(3) Decomposition curves for dilute and concentrated solutions of aluminum bromide in ethyl bromide have been determined, with platinized and with polished platinum electrodes, as well as with aluminum electrodes.

(4) Aluminum has a single potential of  $+1.10 (\pm 0.2)$  volt, neglecting the possible small E. M. F. at the contact of the solutions, against a 40.95 percent solution of aluminum bromide in ethyl bromide; and bromine, a single potential of  $-1.20 (\pm 0.02)$  volt.

(5) A current density of 0.0023 ampere per sq. cm. or about two amperes per sq. ft. is just sufficient to compensate for the solvent action of the solution upon the deposited aluminum in the concentrated solution (40.95 percent). A dilute solution (4.38 percent) failed to yield aluminum even at moderately high current density.

(6) An aluminum anode, which had been stripped of its film electrolytically, gave 2.235 volts in a 4.38 percent solution of aluminum bromide in ethyl bromide against a platinum cathode. Similarly magnesium gave 2.277 volts, from which by subtracting  $+1.20$  for bromine we get 1.08 volts as the approximate single potential of magnesium against this solution.

(7) A striking exception to the Nernst-Thomson rule is cited, in that ethyl bromide with a dielectric constant of 8.9

yields a solution of good conductivity with aluminum bromide as solute.

(8) The bearing of this work upon the aluminum anode phenomena is discussed ; it appears that a film is formed upon aluminum in a solution very free from oxygen, but the high counter pressure mentioned by Isenburg and by Cook for aqueous solutions has not been found thus far.

(9) Aluminum bromide dissolved in ethyl bromide is found to lack the requirements of a commercial plating solution for the deposition of aluminum.

This work has been carried out in the laboratory of physical chemistry. I wish to thank Prof. Louis Kahlenberg for his continued interest in my work and for the many favors conferred upon me during the past two years. I am also indebted to Prof. G. C. Shaad for the adjustment of my potentiometer resistances, and to Prof. C. F. Burgess and Mr. F. L. Shinn for the use of instruments.

*University of Wisconsin,  
June 11, 1904.*

## ACTION OF AMALGAMS UPON SOLUTIONS

(REPLY TO G. MCP. SMITH)

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BY GUSTAVE FERNEKES

In a recent article, G. McP. Smith<sup>1</sup> criticises the explanation given by me of the phenomena described in a paper on the action of sodium and potassium amalgams on various aqueous solutions.<sup>2</sup> Smith in an attempt to harmonize the facts observed by me, with the theory of electrolytic dissociation has drawn some rather hasty conclusions from very meager experimental evidence. In this paper I purpose to show that the great number of experiments which I have performed, and also the few additional ones of Smith, can not only be readily explained without the aid of the electrolytic dissociation theory, but that it is impossible to explain the majority of them by means of that theory.

Smith made potassium amalgam from sodium amalgam, by acting upon the latter with a concentrated solution of potassium chloride; and vice versa he made sodium amalgam from potassium amalgam, treating the latter with a concentrated sodium chloride solution. He further repeated some of the experiments of Schumann,<sup>3</sup> preparing barium and magnesium amalgams from sodium amalgam, by acting upon the latter with solutions of the corresponding salts. The only new fact which Smith has discovered is, that sodium amalgam can be prepared from potassium amalgam by the method described above. Without attempting to make sodium amalgam from calcium, barium or magnesium amalgams, by treating these amalgams with a concentrated sodium chloride solution, Smith nevertheless proceeds to the following general statement,<sup>4</sup> "But nowhere have I seen that sodium amalgam has been prepared from potas-

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<sup>1</sup> Jour. Phys. Chem. 8, 208 (1904).

<sup>2</sup> Ibid. 7, 611 (1903).

<sup>3</sup> Wied. Ann. 43, 101 (1891).

<sup>4</sup> l. c. p. 213.

sium amalgam or from magnesium amalgam, etc., as should be possible according to the ionic theory and the law of mass action."

I repeated Smith's experiments with sodium and potassium amalgams, and obtained the same results which have been mentioned above. I also prepared barium and calcium amalgams in the same manner described by Schumann. I then attempted to replace barium in its amalgam by sodium or potassium, treating the amalgam with a concentrated sodium chloride or potassium chloride solution.

The experiments were performed as follows: 50 g of barium amalgam were placed in an Erlenmeyer flask, and covered with a strong solution of potassium or sodium chloride. The solution was allowed to remain in contact for from four to five hours. The solution was now poured off and the amalgam carefully washed with water. A very dilute hydrochloric acid solution was now poured upon the amalgam until the evolution of gas ceased. After this solution had been poured from the mercury into a beaker, the barium was precipitated by means of dilute sulphuric acid, filtered, ignited and weighed. The filtrate was evaporated to dryness in a platinum dish and the residue weighed. This residue was either sodium or potassium sulphate. A blank experiment was performed with pure barium amalgam.

50 g of the amalgam contained 0.5724 g barium and 0.0160 g sodium. 50 g of this same amalgam after having been treated for four hours with a concentrated sodium chloride solution contained 0.4517 g barium and 0.0131 g sodium. The amalgam when allowed to act on a very concentrated potassium chloride solution for five hours, contained 0.5263 g barium and 0.0138 g potassium. A few more experiments were now performed with solutions of potassium sulphate and also with sodium sulphate. The object in these cases was to throw insoluble barium sulphate out of solution, and thus give the potassium or sodium a better chance to combine with the mercury. The difficulty which presented itself here is quite apparent. Barium sulphate

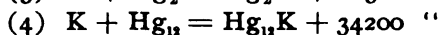
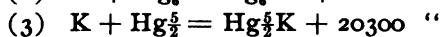
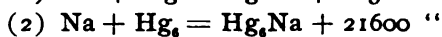
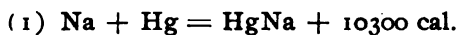
would form at the surface of the amalgam and prevent further action. I therefore shook the amalgam violently with the solution, and continued this shaking with an occasional renewal of the solution until no more turbidity occurred. But when I now examined the amalgam I found neither barium nor alkali metal present. To complete this series of experiments, I tried various temperatures up to  $40^{\circ}\text{C}$  with the same result as above. This shows conclusively that barium in its amalgam is not replaceable by either sodium or potassium by the method which Smith thought possible by the ionic theory. That barium actually acts on the solution is shown by the analyses, but it is also seen that the corresponding quantities of sodium or potassium did not combine with the mercury. It might be added here that I did not attempt to remove the small quantity of sodium in the barium amalgam, because I did not think it would interfere with the outcome of these experiments. In subsequent experiments I removed all but a slight trace of sodium in the amalgam.

As Smith's objections were found not to hold for barium amalgam, it could be used for the purpose of testing the correctness of Prof. Kahlenberg's theory. According to this theory we should expect barium amalgam to act more slowly upon a solution of potassium or sodium chloride than upon pure water, because each molecule of the salt would influence the surrounding molecules of water by chemical attraction. By the ionic theory we should expect no difference in the rate of reaction. It was found that water acted about three times as fast upon barium amalgam as did a solution of potassium chloride.

These facts in themselves are sufficient to prove that the view held by Prof. Kahlenberg is correct. But to show that Smith has omitted consideration of the important factor, chemical attraction, in explaining the replacements in the mercury, I performed another experiment to show how essential this factor is.

A solution containing equimolecular quantities of sodium and potassium chlorides was allowed to act on sodium amalgam.

After fifteen minutes, the amalgam was examined, and found to contain only potassium, although more sodium than potassium was present in the solution at the end of the experiment. The experiment was now performed with potassium amalgam and the same solution. Again only potassium was found in the amalgam. This proves that potassium has a greater affinity for mercury than sodium. This fact is further born out by regarding the heats of formation which it might be well to present in this connection.<sup>1</sup>



It appears from these data that by choosing the potassium or sodium in the proper proportions to the mercury, the heat of formation of the potassium amalgam may be made to exceed that of sodium amalgam or vice versa. This is particularly evident when we regard reactions (2) and (3). From these thermochemical data Berthelot has explained the replacement of sodium in sodium amalgam by potassium in a potassium hydroxide solution, and it did not require the assumption of ions to account for the facts satisfactorily. It is true that the law of mass action asserts itself in these, as in all chemical reactions, but Smith's attention need hardly be called to the fact that this law is entirely independent of the ionic theory, and was known long before that theory existed.

The reason why barium in barium amalgam is not replaced by sodium or potassium from solutions of their salts is perfectly obvious. In the case of barium amalgam there evidently exists a compound whose heat of formation so far exceeds that of either sodium or potassium amalgam, that a replacement by these metals is in no manner possible. We may therefore bring even saturated solutions of sodium or potassium chloride into contact with barium amalgam without effecting a replacement. Calcium will probably act in a similar way to barium. From the fact

<sup>1</sup> Berthelot. *Comptes rendus*, 88, 1335 (1879).



that barium has such a strong affinity for mercury we should expect the vapor tension of the solution of barium in mercury to be depressed correspondingly. In looking over the results obtained<sup>1</sup> for the molecular weight of barium and calcium where mercury was used as a solvent, I found that it was about one-half that obtained by other methods. Ostwald says that he could not harmonize these facts with the existing views. According to Prof. Kahlenberg's theory the explanation is again very simple.

I have thus shown in this paper that the reciprocal replacement of metals in mercury is not always possible as might be expected from "the ionic theory and the law of mass action." That a retardation of the evolution of hydrogen by the action of an amalgam which is not thus replaceable, upon a solution is nevertheless observed. Furthermore the replacements which do take place in the amalgams can be explained on a purely thermochemical basis and the laws of chemical attraction.

But before concluding this paper, it might be well to ask Smith how he would explain by the ionic theory the anomalous behavior of sodium hydroxide solutions towards both sodium and potassium amalgams. These phenomena he seems to have overlooked entirely. Besides this there is still the great number of solutions of organic compounds which he has failed to mention. All the above facts again show how limited the application of the ionic theory is toward the general subject of solutions, and they have tended very much to strengthen my belief in the theory which Prof. Kahlenberg holds.

*Michigan College of Mines,  
Houghton, August, 1904.*

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<sup>1</sup> Ostwald. *Solutions*, p. 193.

## THE BREAKS IN THE SOLUBILITY CURVES

BY W. MEYERHOFFER<sup>1</sup>

In a short note<sup>2</sup> I pointed out that Hermann Kopp in 1840 had stated the theorem that a change in the solid phase occurs at a break in the solubility curve. Professor Ostwald<sup>3</sup> answered this note, disputing an essential part of Kopp's discovery.

Professor Ostwald states first that Gay-Lussac was the discoverer of the breaks and then proceeds as follows: "To him [Gay-Lussac] I believe we must credit the first proof that the apex found by him in the solubility curve of sodium sulphate occurs at the same temperature as the 'melting-point' of Glauber's salt."

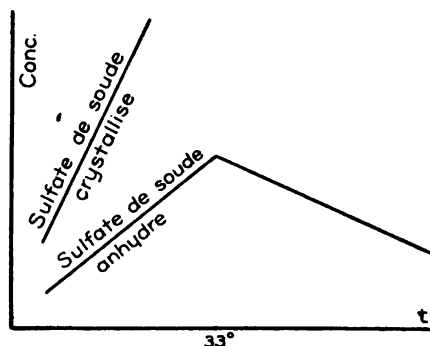


Fig. 1. Drawing of Gay-Lussac

Now there is no doubt that Gay-Lussac determined the break empirically, a fact which I have already pointed out in my note. On the other hand I believe that he did not establish any real relation between the break and the melting-point of Glauber's salt. In proof of this I quote the passage on the solubility of  $\text{Na}_2\text{SO}_4$  from the well-known paper of Gay-Lussac.<sup>4</sup> His diagram is also given schematically in Fig. 1.

<sup>1</sup> Translated by W. D. Bancroft.

<sup>2</sup> Zeit. phys. Chem. (11) 42, 501 (1903).

<sup>3</sup> Ibid. 42, 503 (1903).

<sup>4</sup> Ann. Chim. Phys. (2) 11, 313 (1819).

"On voit par ces résultats que la solubilité du sulfate de soude suit une marche très singulière. Après avoir augmenté rapidement jusqu'à la température d'environ  $33^{\circ}$ , où elle a son *maximum*, elle va en diminuant jusqu' à  $103.17^{\circ}$ , et à ce terme, elle est à-peu-près la même que celle qui correspond à  $30.5^{\circ}$ . Le sulfate de soude offre le second exemple d'un corps dont la solubilité décroît lorsque la température augmente, à partir d'un certain terme, car M. Dalton a déjà reconnu à la chaux la même propriété. On a tracé dans la planche la ligne de solubilité de sulfate anhydre; elle est formée par deux branches convexes vers l'axe des abscisses, ayant un point de rebroussement correspondant à-peu-près à la température  $33^{\circ}$ . On n'a pu représenter qu'une petite portion de la ligne de solubilité du sulfate cristallisé à cause de l'étendue des ordonnées: cette ligne ne pourrait d'ailleurs servir au-delà de  $50^{\circ}$  parceque le sulfate de soude ne retient plus alors une quantité d'eau aussi considérable que dans les températures basses."

From this passage it appears that Gay-Lussac speaks only of one solubility of sodium sulphate. It has a maximum at  $33^{\circ}$  which appears in the drawing as a break (point de rebroussement). At  $50^{\circ}$  a lower hydrate is said to appear and one cannot express the solubility above  $50^{\circ}$  in terms of Glauber's salt. If one were to be logical, the solubility below  $50^{\circ}$  ought not to be referred to the anhydride. The fact that Gay-Lussac does this shows that he was not clear in regard to the phenomena. He certainly knew nothing about a coincidence between the break and an inversion temperature.

Even in 1835 Berzelius was not quite clear in regard to these matters. Berzelius<sup>1</sup> knew that below  $33^{\circ}$  the salt crystallizing is different from the one separating above that temperature. He says however later: "100 Tl.  $H_2O$  von  $32^{\circ}$  lösen 270 Tl., von  $33^{\circ}$  322 Tl. schwefelsaures Natron<sup>2</sup> auf. Wird die bei dieser Temperatur gesättigte Lösung erwärmt, so vermin-

<sup>1</sup> Lehrbuch der Chemie von Berzelius-Wöhler. Third Ed., Vol. 4. Dresden and Leipzig, 1835, 4 Bd.

<sup>2</sup> Glauber's salt is meant.

dert sich das Lösungsvermögen des Wassers und das Salz setzt sich ab, so das bei 50° die Flüssigkeit nur 262 Tl. Salz auf 100 Tl. Wasser aufgelöst enthält. Geschieht diese Erwärmung sehr langsam so schießt das wasserfreie Salz daraus an."

From the fact that Berzelius gives the solubility data at 50° with reference to Glauber's salt, it is very clear that he considered the maximum as the property of *a single substance*, just as Gay-Lussac had done sixteen years earlier. On the other hand Kopp recognized clearly that it was a case of the solubility curves of *two different salts*, the two curves having one point in common. In addition he identified the temperature of this point with the melting-point of Glauber's salt and thus expressed nearly everything which the doctrine of heterogeneous equilibrium has to say about this case. There is of course no doubt that he had a false conception of the state of the salts in the solution. Is the credit of a discovery diminished because the investigator remains in error with regard to another point which has only a slight bearing on the discovery? I say "remains in error" because Kopp's mistake is not due to false conceptions or conclusions, but arises entirely from the fact that Kopp kept to the views and methods of expression which were in use before him. Who can guarantee that, in stating new scientific truths, we ourselves may not make use of expressions which have come down to us and which a later time will find inaccurate?

I have since become familiar with a second paper of Gay-Lussac's<sup>1</sup> in which there is also something on the solubility of

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<sup>1</sup> Considérations sur les Forces chimiques. Premier Mémoire: Sur la Cohésion. Ann. Chim. Phys. 70, 402 (1839). The study of this noteworthy paper is to be recommended to those writing the history of our science. In addition to the questions discussed in the text, this article contains a series of interesting comments, among others the observation *that the vapor-pressure is the same above solid and liquid*. The author confirms this on water and on HCN (p. 420). The solubilities change regularly when the solid phase changes to liquid (p. 423). It is shown that a solution boiling above 100°, at 110° for instance, gives off a vapor having this temperature and not that of 100° (p. 420, note). Finally there is also the remark that anhydrous salts dissolve with absorption of heat only if they form no hydrates; otherwise with evolution of heat (p. 426).

sodium sulphate. The author recognizes that there is a close relation *between the readiness of vaporization of a substance and its solubility*. Now the vapor pressure is independent of the state of a substance or of the "cohesion" of its molecules since it remains constant when the substance changes for instance from the solid to the liquid state. The solubility should therefore be independent of the cohesion. This suggests the question why the pressure increases with rising temperature while some salts, such as sodium sulphate or sodium selenate, show a sudden break and a decreasing solubility.

The author answers the question, which has been raised, in the following manner (p. 426): " \* \* \* as a first assumption the breaks in the solubility curves of some substances can easily be accounted for in that *at this point it is no longer the same substance which dissolves further*. Thus the solubility of chlorine increases between  $0^{\circ}$  and  $8^{\circ}$ , the interval in which chlorine occurs as hydrate. At  $8^{\circ}$  the hydrate decomposes and the solubility at once begins to decrease, becoming practically zero at  $100^{\circ}$ . *It is obviously chlorine hydrate which dissolves between  $0^{\circ}$  and  $8^{\circ}$  and chlorine alone above this temperature*. As for sodium sulphate, its decreasing solubility as the temperature rises above  $33^{\circ}$  can be referred to a decrease in the affinity. I shall come back to the solubility of this salt."

This continuation did not appear any more than did the promised sequel to the famous memoirs of 1819.

The passages which I have italicized prove that the conception of different solubility curves, which Kopp formulated clearly a year later, was no longer entirely strange to the great French investigator. He refers however to chlorine hydrate, and Roozeboom has shown us that it is only in open vessels that we cannot determine the solubility of this compound above  $8^{\circ}$ . As a matter of fact this hydrate can exist up to  $28.7^{\circ}$ . The decomposition at  $8^{\circ}$  is not due to the formation of a new phase, but to the fact that the vapor-pressure of the solution exceeds one atmosphere. At  $8^{\circ}$  it is not two solubility curves

which intersect but a solubility curve and an absorption curve.<sup>1</sup> It is surprising that Gay-Lussac has no explanation for the behavior of sodium sulphate. It is clear that he did not know that Glauber's salt is decomposed at 33°. Otherwise he would certainly not have hesitated to extend to sodium sulphate what he had said about chlorine hydrate. This reference disproves once more the assumption that Gay-Lussac had recognized the second significance of the temperature of 33°. The passage I have quoted proves beyond a question that Gay-Lussac had some share in the generalization which Kopp soon afterwards formulated more exactly. It is further of interest that in the report on Gay-Lussac's paper Berzelius<sup>2</sup> drew the natural conclusion in regard to Glauber's salt which Gay-Lussac had failed to draw. He says: "Gay-Lussac offers no explanation for the behavior of Glauber's salt solution and is to take up this point later. The explanation is, however, exactly the same. The hydrated sodium sulphate ceases to exist above the temperature at which the solubility becomes a maximum."

After this utterance one might have expected that Berzelius would have devoted a few words to the formulation of the same idea by Kopp.<sup>3</sup> This was not the case. In the next year-book Berzelius<sup>4</sup> mentions Kopp's paper but does not go into the question of sodium sulphate. Perhaps this omission may have had something to do with Kopp's results remaining unnoticed.

*Berlin-Wilmersdorf,  
June 24, 1904.*

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<sup>1</sup> This latter curve of course represents also a univariant system in spite of there being two components in two phase. The limitation  $p = 1$  atm reduces the degrees of freedom to one.

<sup>2</sup> Berzelius. Jahresber. über die Fortsetz. der physikalischen Wissenschaften. Deutsch von Wöhler, 2, 39 (1841).

<sup>3</sup> Liebig's Ann. 34, 260 (1840).

<sup>4</sup> Jahresber. 21, 121 (1842).

## NEW BOOKS

**Thermodynamique. I. Notions Fondamentales.** By L. Marchis. *Préface de P. Duhem.* (*Bibliothèque de l'Élève Ingénieur.*) 16 × 25 cm; pp. 176. Grenoble: A. Gratier and J. Rey; Paris: Gauthier-Villars, 1904. Price: paper, 5 francs. — The *Bibliothèque de l'Élève Ingénieur*, in which series the present work appears, is a collection of short introductory treatises on various special subjects of interest to engineers. Marchis's book supplies the treatment of thermodynamics, the present first volume being concerned with the general principles of this science. The subject-matter is arranged in five chapters: Equivalence of Heat and Work, The Principle of Carnot-Clausius, Entropy, Utilizable Energy, Chemical Heat and Voltaic Heat. Applications of the principles are to appear in a second volume on the thermodynamics of fluids. The book is a very carefully written elementary exposition, and is introduced by a long and interesting preface by Duhem. The typography calls for comment; ill-arranged, and loaded with italic and heavy-face type, it is unqualifiedly bad. Usually they do these things better in France.

J. E. Trevor

**Applications of the Kinetic Theory to Gases, Vapors, Pure Liquids, and the Theory of Solutions.** By William Pingry Boynton. 13 × 19 cm; pp. x + 288. New York: The Macmillan Company, 1904. — From this book, which is the outcome of a course of lectures given in the University of California, a fair idea of the character and content of the kinetic theory of fluids can be gained with but little trouble. The author has attempted only a sketch of the subject, but he has made this sketch lucid, well arranged, and decidedly interesting. His general attitude is indicated by the remark that "the object of our treatment is not argumentative, so that for the present it is immaterial whether the theory be regarded as a statement of what actually occurs, or simply as a mechanical analogy." The topics treated are ideal gases, gases whose molecules have dimensions, conduction of electricity and of heat and diffusion, etc., the van der Waals equation, vaporization, liquids, solutions, the theory of dissociation.

J. E. Trevor

**La Mécanique, exposé historique et critique de son développement.** By Ernst Mach. *Ouvrage traduit sur la quatrième édition allemande par Emile Bertrand. Avec une Introduction de Emile Picard.* 16 × 25 cm; pp. ix + 498. Paris: A. Hermann, 1904. Price: paper, 15 francs. — At various times, on the appearance of successive German and American editions of Mach's famous *Mechanics*, we have given expression to the gratification naturally aroused by the growing popularity of this wonderfully clear and inspiring book. Every one concerned is now to be congratulated on the issue of a carefully prepared French version. The value of this edition is considerably enhanced by its special introduction, a thoughtful essay, by Picard, on the bearing of the historical study of the development of mechanics.

J. E. Trevor

**Carl Anton Bjerknes.** *Gedächtnisrede gehalten vor der Gesellschaft der Wissenschaften zu Christiania am 17. April, 1903.* By V. Bjerknes. 15 X 23 cm; pp. 31. Leipzig: Johann Ambrosius Barth, 1904. Price: paper, 1.20 marks. — This small brochure, in which the younger Bjerknes celebrates the scientific labors of his father, is extremely interesting. C. A. Bjerknes, famous for his hydrodynamical researches, came of a family of Norwegian peasants. On leaving the university he became a sort of police-watchman at a silver mine. Here he studied mathematics in his free time, and won the gold medal of a mathematical prize competition. This led to his incumbency of a traveling fellowship, on which he studied in Paris and Göttingen. Dirichlet's announcement, at Göttingen, of his discovery that a frictionless fluid offers no resistance to the uniform motion of a solid sphere, suggested to Bjerknes the investigation of the mutual influence of the motions of two such spheres. The remainder of a long life was occupied by this investigation, the outcome of which was the establishment of a remarkably deep-seated analogy between the details of electric and hydrodynamic phenomena. A notice of the two-volume work in which the publication of these researches has been begun may be found in this Journal, 4, 394 (1900); 7, 219 (1903). The brochure before us gives an unaffected and most fascinating account of this life and work; it is quite the model of what such an address should be. It is illustrated by a handsomely executed photogravure portrait.

J. E. Trevor

**Rayons "N".** By R. Blondlot. (*Actualités Scientifiques.*) 12 X 19 cm; pp. vi + 76. Paris: Gauthier-Villars, 1904. Price: paper, 2 francs. — This is a reprint of Blondlot's papers on the much maligned, one might almost say notorious, "N"-rays. It begins with a paper detecting a kind of polarization in the X-rays by a linear spark explorer made to lie normally to the plane of the cathode and X-rays. Crystals like sugar and quartz rotate this plane, mica produces elliptic polarization (tested independently by the Babinet compensator), a quartz prism produces refraction, a quartz lens brings the X-rays to a focus, ground glass diffuses them, etc. Blondlot concludes that there is a new kind of radiation polarized in the plane of emission, penetrating aluminum and black paper, but differing from the X-ray in being refrangible and in not producing fluorescence or photographic effect. Their refractive index places them near Rubens's *Reststrahlen*, and this induces Blondlot to look for "N"-rays coming from an incandescent Welsbach mantle. The quest, using his spark explorer is successful; but the rays differ from Rubens's radiation in not passing through salt, water, glass, etc. Flames, incandescent metals, even the sun, emit "N"-rays of varying indices (1.5-3). A Nernst burner is particularly active.

Subsequently he finds that a little flame may replace the spark gap as an explorer, but without showing the polarization of the rays. Incandescent metal is similarly indicative. Though "N"-rays cannot excite phosphorescence, they augment it similarly to the ultra-red rays, and the effect is in no case simply thermal.

Pursuing these experiments further, Blondlot now finds that faintly illuminated paper or even reflected light is enforced by the "N"-rays. Quartz



and other minerals become secondarily active. Dry rock and gravel exposed to the sun are a source of "N"-rays. In all cases the activity is gradually assumed and gradually decays. Whereas a mere film of pure water cuts off the rays unconditionally, salt water is transparent to them and even becomes secondarily active.

Again he finds that wood, glass, etc., under compression emit "N"-rays; and, more remarkably still, unannealed glass and metal are permanent sources. To determine the dispersion he employs a Nernst lamp producer, properly screened and provided with aluminum windows, lenses or prisms and grating, in the usual way. The refractive indices 1.04 to 1.85 are obtained. Using a grating or a Newton ring method in a determinate part of the "N"-spectrum, he finds wave-lengths from 0.000008 cm to 0.000018 cm. Contrary to his original inferences (see above), these rays are therefore ultra-violet, but they are not absorbed by air as are the Schumann rays.

Very interesting photographs show the property of the "N"-rays to intensify the spark. In this way Blondlot obtains objective evidence verifying most of his subjective impressions. Finally a new type of radiation called " $N_1$ " is discovered, which tends to darken and not to intensify his spark or flame explorer. The refractive indices were very nearly 1 (1.004-1.011) and the wave-lengths 0.008 $\mu$ -0.003 $\mu$ .

The book reads from cover to cover like a fairy tale, or more perhaps like a jeu d'esprit of President Jordan. It seems impossible that a physicist of Blondlot's acuteness and experience can have been misled in these splendidly devised experiments. And yet Blondlot seems still to hold the monopoly of the "N"-rays in his own hands.

C. Barus

**Le Radium, la Radioactivité.** By Paul Besson. *Avec une Préface du A. d'Arsonval.* (*Actualités Scientifiques.*) 12 X 19 cm; pp. xii + 172. Paris: Gautier-Villars, 1904. Price: paper, 2.75 francs. — The present little book is a straightforward account of radioactivity (so named by Curie), giving an accurate history of the subject together with the efficient methods of investigation. The chemical part of the book should be authoritative, inasmuch as M. Besson collaborated with the Curies in the commercial manufacture of radioactive preparations. But there is not much detail.

The subjects principally discussed are naturally those in which the Curies and other French investigators have been most active. In comparison with J. J. Thomson's recent book, the text seems now antiquated. The information given, however, is precise. The larger interests of the authors seem to be centered in the medical applications which make up a considerable part of the volume, and these will be read even by laymen with profit.

C. Barus

**Die elektrochemische Industrie Deutschlands.** By P. Ferchland. (*Monographien über angewandte Elektrochemie. XII. Band.*) 16 X 24 cm; pp. viii + 66. Halle: Wilhelm Knapp, 1904. Price: paper, 2.50 marks. — The arrangement of the subject is as follows: historical introduction; production of power; alkali and chlorine; electrical bleach; hydrogen, oxygen and ozone; calcium carbide and phosphorus; sodium, magnesium and aluminum; zinc; copper and nickel; noble metals; other inorganic processes; organic

electrochemistry. The author's view in regard to industrial organic electrochemistry is that there is no such thing and that there is no prospect that there ever will be. This is not the orthodox view, but the author's statement of facts seems fairly conclusive.

The general attitude of the author is shown by this quotation: "The real field for electrolysis is in the preparation of the light metals and their salts. The great stability of these salts makes their decomposition or change by ordinary methods either impossible or very difficult, so that electrolysis is often the only or the cheapest way in spite of the losses in the creation of electrical energy."

A number of pages are devoted to proving that the Griesheim-Elektron process for making caustic and bleach is better than the Castner process. In spite of this there is nothing to show what the former process actually is. It has been stated apparently on good authority that it is a mercury process. If true, this plays havoc with the author's argument.

Wilder D. Bancroft

*Éléments de Chimie Inorganique.* By W. Ostwald. Traduits de l'Allemand par L. Lazard. Première Partie: Métalloïdes. 16 X 25 cm; pp. xi + 542. Paris: Gauthier-Villars, 1904. Price: paper, 15 francs. — Although this translation is based officially on the first German edition, it yet has in it most of the corrections made in the second edition. It is with great pleasure that we welcome the invasion of France by Ostwald's books. The translation has been well done. The type is perhaps a little small, but the general effect of the page is excellent.

Wilder D. Bancroft

*Die Beziehungen zwischen Äquivalentvolumen und Atomgewicht.* By W. Borchers. 16 X 24 cm; pp. 17. Halle: Wilhelm Knapp, 1904. Price: paper, 0.80 mark. — Instead of plotting atomic volumes against atomic weights, the author plots equivalent volumes and claims to get a more regular curve. A discussion of the resulting curve leads the author to predict the existence of a number of new elements.

Wilder D. Bancroft

*A Laboratory Manual of Organic Chemistry for Beginners.* By A. F. Holleman. An Appendix to the Author's Text-book of Organic Chemistry. Translated from the Dutch by A. Jamieson Walker, with the co-operation of the author. 12 X 20 cm; pp. xiv + 78. New York: John Wiley and Sons, 1904. Price: bound, \$1.00, net. — In the preface the author says: "A student beginning the study of organic chemistry usually has to content himself with text-books and lectures, and very seldom has the opportunity of handling the compounds about which he has to read." Such a state of things does not occur in this country, and the more quantitative manuals now in use are not likely to be displaced by this essentially qualitative book. On the other hand, the volume could be used with great advantage as a manual for lecture experiments. From this point of view, the book is an excellent one.

Wilder D. Bancroft

## REVIEWS

*The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry*

### General

**Note on the comparison of the meter with the wave-length of light.** *O. Chwolson. Boltzmann's Festschrift, 28 (1904).*—Attention is called to the possibility of any given ray of light changing its wave-length in time. The wave-length depends on the 'density' of the ether. If the ether is not homogeneous or if its properties vary with time, the wave-length will also vary. While there is no reason to suppose that this will happen, there is no way of proving that it will not. *W. D. B.*

**The mechanical significance of the temperature and entropy.** *M. Planck. Boltzmann's Festschrift, 113 (1904).*—A discussion of Boltzmann's and Gibbs's definitions of the entropy. The conclusion reached is that the Boltzmann definition is the more general and the better because it includes irreversible phenomena. *W. D. B.*

**Effect of change of specific heat on inversion work.** *J. H. van't Hoff. Boltzmann's Festschrift, 233 (1904).*—As a result of Richards's work on the change of the specific heat with the temperature, the author writes the formula for the relation between the free energy and the heat effect

$$\frac{dE}{dT} = \frac{E - Q_0}{T} - S,$$

where  $Q_0$  is the heat effect at the absolute zero and  $S$  is the difference between the specific heats of the two systems. It is assumed that  $S$  is not a function of the temperature. A further deduction is that, for inversions without concentration changes, the ratio of  $dE/dT$  to  $S$  should be  $-6.7$ . The figures given by Richards vary from  $-5$  to  $-8$ . The author believes that this is due to experimental error, but it seems equally probable that there is an error in the assumption that  $S$  is not a temperature function. The extra term due to the difference in the specific heats of two systems accounts possibly for the dissociation of endothermal substances at high temperatures. *W. D. B.*

**Apparatus for representing the kinetic theory of heat.** *L. Pfandler. Boltzmann's Festschrift, 71 (1904).*—Two pieces of apparatus are described. The first shows: the movement of like gas molecules in a vessel with heated walls; the gradual heating of a gas from the absolute zero through the walls of the containing vessel; condensation of vapors; diffusion; two gases with different molecular weights; action of gravity on a gas. The second shows heat conduction in a solid body. *W. D. B.*

**On congruent and incongruent fusion of double salts.** *W. Meyerhoffer. Zeit. phys. Chem.* 48, 109 (1904). — If a solution will not solidify without change of temperature, it obviously cannot be prepared by fusion of any mixture of the solid phases separating from it at that temperature. Such a melt is called incongruent. All minimum and maximum freezing-points correspond to congruent melts; all others to incongruent melts. The solution in equilibrium with hydrated and anhydrous sodium sulphate and vapor is incongruent because it contains more water even than the hydrated salt and could not therefore be prepared from any mixture of hydrated and anhydrous sodium sulphate.

The author calls attention to the fact that the number of components changes if water reacts with a salt producing basic and acid compounds. He admits that this has been known for many years; but seems to think that it has not been stated so clearly before. *W. D. B.*

**The specific heats and electrical conductivities of some sulphides.** *F. Streintz. Boltzmann's Festschrift, 196 (1904).* — The specific heat of fused and cast lead sulphide is 0.0529, while the crystallized sulphide has a value of 0.0557, and the powdered sulphide gives a value of 0.0601, increasing to 0.0648 when the powder is put under great pressure. Amorphous lead sulphide has a specific heat of 0.117. The fused and cast sulphide conducts electricity well while the amorphous sulphide is a poor conductor. Crystallized mercury sulphide has a specific heat of 0.0548 and the black amorphous sulphide of 0.1026. The amorphous sulphide, however, conducts electricity better than the other. With silver sulphide, marked hysteresis effects were observed. *W. D. B.*

**Heats of combustion of some polymeric and isomeric compounds formed by light.** *C. N. Rüber and J. Schetelig. Zeit. phys. Chem.* 48, 345 (1904). — Cinnamic acid is changed by light into  $\alpha$ -truxillic acid; and cinnamylidene malonic acid into a polymeric form. In neither case could a change in the heat of combustion be detected. On the other hand, there is a difference of 8.9 Cal between the heats of combustion of allocinnamylidene acetic acid and cinnamylidene acetic acid. The chemical change in this latter case is believed to be analogous to the change of maleic into fumaric acid. *W. D. B.*

**Contribution to the stereochemistry of carbon compounds, especially unsaturated ones.** *P. Pfeiffer. Zeit. phys. Chem.* 48, 40 (1904). — The chemical behavior of unsaturated isomers is often in flat contradiction with the predictions from the stereochemical formulas. The author assumes that the most stable form of a  $C_4R_6$  compound is that which is most nearly octahedral. He also treats the  $C_3$  as a unit with the coordinate number six. The paper is an attempt to prove that these assumptions suffice to explain all the known discrepancies. *W. D. B.*

#### One-Component Systems

**Physical-chemical studies on tin, V.** *E. Cohen. Zeit. phys. Chem.* 48, 243 (1904). — The mean temperature in Ohlau in Silesia is  $+8^\circ$ . Under the wooden roof of the church is an organ in which the pipes have been corroded

to an extraordinary degree by the so-called tin pest; in other words by the change to the stable form. *W. D. B.*

**The freezing-point of nitrobenzene.** *F. C. C. Hansen. Zeit. phys. Chem.* 48, 593 (1904). — The freezing-point of nitrobenzene is usually given as  $5.3^{\circ}$ . It is found that the anhydrous acid melts at about  $5.7^{\circ}$ , but that it soon absorbs moisture enough from the air to lower the freezing-point to  $5.25^{\circ}$ . The quadruple point was not determined. The freezing-point of benzene under similar circumstances drops from  $5.54^{\circ}$  to  $5.47^{\circ}$ . *W. D. B.*

**Spontaneous crystallization of supercooled liquids.** *C. Fuchtbauer. Zeit. phys. Chem.* 48, 549 (1904). — A study of the behavior of supercooled liquids with special reference to the limits of the metastable state. It was not found possible to obtain concordant results. Special experiments on solutions of liquids in liquids led to the conclusion that supersaturation phenomena would be observed if all dust should be removed. *W. D. B.*

**On the vapor-pressure of mercury at ordinary temperatures.** *E. W. Morley. Phil. Mag.* [6] 7, 662; *Zeit. phys. Chem.* 49, 95 (1904). — Air was bubbled through mercury, and the loss of mercury was determined by weighing. One experiment is cited to show that the air was saturated with mercury vapor. The vapor-pressures in millimeters are 0.0010 at  $16^{\circ}$ , 0.0027 at  $30^{\circ}$ , 0.0052 at  $40^{\circ}$ , 0.0113 at  $50^{\circ}$ , 0.0214 at  $60^{\circ}$ , and 0.0404 at  $70^{\circ}$ . *W. D. B.*

**An application of the method of Caillietet and Mathias to the determination of the critical volume.** *M. Centnerzwer. Zeit. phys. Chem.* 49, 199 (1904). — If we have a known weight of liquid in a known volume and determine the temperature at which one of the phases disappears, we have the actual density of the phase remaining. The author makes a series of measurements with varying amounts of liquid and plots the results. By extrapolation and by assuming the law of the rectilinear diameter, he obtains both the critical temperature and the critical volume. *W. D. B.*

**The expansion work of a dissociating gas.** *J. E. Trevor. Boltzmann's Festschrift*, 493 (1904). — Starting with an ideal gas dissociating into ideal gases, the author calculates the expansion-work of the gas between given limits of the degree of its dissociation and the expansion-work when the temperature is changed under the condition of a constant degree of dissociation being maintained. *W. D. B.*

**A method for determining vapor-densities by increase of pressure and its relative accuracy.** *W. Haupt. Zeit. phys. Chem.* 48, 713 (1904). — The author describes an apparatus for measuring the change of pressure when a known weight of substance is vaporized in a known volume at a known temperature. It is claimed that the method is fully as accurate as the V. Meyer or the Dumas method. *W. D. B.*

**The change in the value of  $b$  in the equation of state as an apparent decrease of the molecule.** *J. D. van der Waals. Boltzmann's Festschrift*, 305 (1904). — The changes in  $b$  in the van der Waals equation may be due to an actual decrease in the size of the molecule or to an apparent decrease due to an

overlapping of the "spheres of influence." The first alternative has previously been discussed and the second forms the subject of this paper. *W. D. B.*

**The atomic and molecular space.** *J. Traube. Boltzmann's Festschrift, 430 (1903).* — This is a brief sketch of the author's previous work. The author discusses the relation of  $b$  to the index of refraction and touches briefly on the difference between gas molecules and liquid molecules. The second half of the paper is given up to the covolume,  $v - b$ . From the value of this he deduces the molecular weight of pure solids. Attention is called to the relation between  $a/v^2$  and the moduli of hardness and elasticity for metals. The formula of van der Waals is believed to hold for solids. *W. D. B.*

**The specific heat of liquids at low temperatures.** *J. J. van Laar. Boltzmann's Festschrift, 316 (1904).* — For liquids at low temperatures the author obtains the equation

$$\left(p + \frac{a}{v^2}\right)(v - b_0) = RT(2 - Z^2),$$

where

$$\frac{b - b_0}{bg - b_0} = Z.$$

The bulk of the paper is taken up by a discussion of  $C_v$ . It is shown that near the freezing-point  $C_v$  is larger for the liquid than for the solid. The specific heat of solids is believed by the author to exclude the possibility of the equation for the solid resembling the equation for liquid or gas. *W. D. B.*

**Study of thin films of copper obtained by ionoplasty.** *L. Houlléviq. Boltzmann's Festschrift, 62 (1904).* — A copper film was deposited on glass by means of the cathode discharge. When the thickness of this film is less than  $40\mu$ , the copper does not react with the vapor of iodine, although it can be made to react with oxygen. This is a most interesting result. It should be confirmed independently and studied more in detail, special stress being laid on the temperature, pressure and nature of the reacting gas. *W. D. B.*

#### Two-Component Systems

**Equilibrium between ammonium and silver nitrates.** *J. v. Zawidski. Zeit. phys. Chem. 47, 721 (1904).* — Silver nitrate and ammonium nitrate do not form mix-crystals as believed by Retgers. There is however a compound  $\text{AgNO}_3 \cdot \text{NH}_4\text{NO}_3$  stable at its melting-point. The author has determined the whole freezing-point curve. The branch for pure silver nitrate as solid phase meets the branch for the double salt almost exactly at fifty molecular percent.

*W. D. B.*

**The formation and change of fluid mix-crystals.** *A. C. de Kock. Zeit. phys. Chem. 48, 129 (1904).* — The author has studied the system *p*-azoxyanisol and *p*-methoxy cinnamic acid. Both substances form fluid crystals and there is a continuous series of fluid mix-crystals, though the so-called solid crystals do not crystallize together. A study was also made of the system *p*-azoxyanisol and hydroquinone. Hydroquinone forms no fluid crystals but it dissolves to a certain extent in the fluid crystals of the other component. The system

*p*-methoxy cinnamic acid and hydroquinone is similar to the preceding one; so is the system *p*-azoxyanisol and benzophenone. The system ethyl *p*-azoxybenzoate and ethyl *p*-azobenzoate present some difficulties which call for further study.

All the results obtained point to the conclusion that the fluid crystals are a homogeneous phase and not an emulsion. The author obtained a sample of Tammann's *p*-azoxyanisol and found that it behaved differently from his own, apparently owing to the presence of some impurity. The only point for which no satisfactory explanation can yet be given is as to the cloudiness of the fluid crystals.

W. D. B.

**Freezing-temperatures of solutions as constant temperatures.** *K. Prytz. Zeit. phys. Chem.* 47, 729 (1904). — A cooled solution is run through ice in a vacuum tube until no further change in temperature takes place. The solution and ice are then in equilibrium. This method appears to call for a fairly large amount of solution, though this could be decreased by cooling both the solution and the ice in advance practically to the right temperature. Special experiments showed that the constant temperature remained the same, even when the rate of flow varied very much.

W. D. B.

**The solubility of  $\beta$ -l-asparagine and of  $\beta$ -l-asparaginic acid.** *H. W. Bresler. Zeit. phys. Chem.* 47, 611 (1904). — The author has determined the solubility in water of asparagine and of asparaginic acid between 0° and 100°. The resulting curves are said to be hyperbolas asymptotic to lines cutting the axis of abscissas at 80°.

W. D. B.

**Theory of saturation phenomena in binary mixtures.** *P. Boedke. Zeit. phys. Chem.* 48, 330 (1904). — This is a paper carried out under Planck's supervision. Formulas are deduced for binary dineric systems, starting with Rothmund's extension of the law of the rectilinear diameter. The conclusions reached are confirmed for the most part by Rothmund's results.

W. D. B.

**Liquefaction of gas mixtures.** *F. Caubet. Zeit. phys. Chem.* 49, 101 (1904). — This is a study of mixtures of nitrous oxide and carbon dioxide, a pair giving a maximum pressure for a certain mixture at each temperature.

W. D. B.

**The nature of liquid air.** *D. A. Goldhammer. Boltzmann's Festschrift*, 410 (1904). — Fisher and Alt applied the van't Hoff-Raoult formula improperly to liquid air because they overlooked the fact that they were dealing with two volatile components. The author has taken into account the partial pressures and finds that the formula holds well for oxygen dissolved in nitrogen, but not for nitrogen dissolved in oxygen. He attributes this discrepancy to experimental error (1 percent) on the part of Baly. He considers it proved that liquid air is a solution. [It would be interesting to know what else liquid air could be.]

Taking the heat of sublimation of nitrogen as 80 cal, the author calculates that the limiting height of the earth's atmosphere could not exceed about 70 kilometers if the atmosphere were moist nitrogen or moist oxygen only. The observations on shooting-stars call for a height of 200 kilometers. On the basis

of the author's calculations this would mean a heat of solution for nitrogen in oxygen of several hundred calories. It is not yet known whether this assumption is correct.

W. D. B.

**The theory of distillation of mixtures.** *J. P. Kuenen. Boltzmann's Festschrift, 483 (1904).* — If a binary solution be boiled in a flask with a reverse cooler so that nothing escapes, a stationary state must finally occur provided the heating and cooling be uniform. The condition for a stationary state is that at any cross-section of the reverse cooler the ascending vapor shall have the same composition as the descending liquid. Under these circumstances liquid and vapor cannot be in equilibrium.

If distillation occurs there is no stationary state and the descending liquid will be poorer in the more volatile component or mixture than the ascending vapor. Even so, the liquid and vapor will only rarely, possibly never, be in actual equilibrium.

W. D. B.

**The vapor-pressures of liquid mixtures, assuming a partially dissociated compound.** *J. J. van Laar. Zeit. phys. Chem. 47, 129 (1904).* — A discussion of the general types of pressure-concentration curves for two liquids which may form a more or less completely dissociated compound. Special reference is made to the case of bromine and iodine. The reviewer feels that most of the mathematics is purely formal and might well have been omitted. The author does not discuss cases in which maxima and minima occur. He also does not consider the relative solubilities of the compound and the components.

W. D. B.

**On Regnault's law.** *P. Duhem. Zeit. phys. Chem. 48, 241 (1904).* — A reply to Zawidski (8, 223).

W. D. B.

**A method for determining the specific weight of very dilute solutions.** *G. Mie. Boltzmann's Festschrift, 326 (1904).* — As the immersion substance the author uses a large thin-walled glass vessel filled full of water. Under these circumstances an error in the temperature determination has only a slight effect.

W. D. B.

**Densities and heat expansion of solutions of naphthalene in different organic solvents.** *C. Forch. Boltzmann's Festschrift, 696 (1904).* — Density determinations for different concentrations of naphthalene in chloroform, toluene, carbon bisulphide and ether. In all cases there is an expansion. The solvents were used as bought, without further purification.

W. D. B.

**Note on the Soret phenomenon.** *W. D. Bancroft. Boltzmann's Festschrift, 553 (1904).* — The Soret phenomenon was explained by van 't Hoff on the assumption that equilibrium is reached when the osmotic pressure of the solute is the same in both parts of the tube. Since the diffusion of the solute to the colder portion must usually be accompanied by a displacement of the solvent, the conclusion of van 't Hoff can hold only for such dilute solutions that the volume occupied by the solute can be neglected. The real conditions for equilibrium have never been formulated.

W. D. B.



*Multi-Component Systems*

The distribution of an undissociated substance. *G. Jaeger. Boltzmann's Festschrift, 313 (1904).* — Starting from the kinetic theory, the author deduces the formula

$$\log \frac{N}{N'} = \frac{rJ}{RT}$$

for the distribution of a substance between two solvents whose mutual solubilities are small. In this equation  $N$  and  $N'$  are the concentrations,  $J$  is the mechanical equivalent, and  $r$  is the difference of the heats of solution in the two solvents. When the solutions are so dilute that the heat of dilution becomes zero,  $r$  is independent of the absolute concentration and the equation becomes

$$N/N' = \text{const.}$$

The author has ignored the solvent action due to the third component, which is never zero. Although the formula is ostensibly more general than the Nernst formula, the author apparently has no intention of checking it by substituting the value of  $r$ . It is a pity that he should not do this because this formula, if correct, would give us the means of calculating distribution coefficients in absolute value. Until this test is made, no one knows anything about the formula. W. D. B.

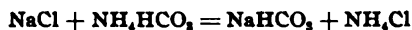
Effect of differently dissociated substances on the solubility of hydrogen and nitrous oxide in water. *W. Knopp. Zeit. phys. Chem. 48, 97 (1904).* — Potassium, sodium and ammonium nitrates decrease the solubility of hydrogen in water. Potassium chloride has the same effect. The highest concentrations were about double normal. The solubility of hydrogen is decreased slightly by chloral hydrate up to concentrations of about double normal. For higher concentrations there is increasing solubility. [The author says that chloral hydrate affects the solubility but little.] Addition of chloral hydrate increases the solubility of nitrous oxide. For some reason this experiment was not carried as far as the corresponding one with hydrogen. Addition of propionic acid also increases the solubility of nitrous oxide, while potassium and sodium nitrates decrease it. The author decides that, on the whole, the results confirm the theory. It would have been just as easy to have reached the opposite conclusion. One of the rules of the game, however, is that only favorable facts count. W. D. B.

The action of carbon dioxide on borax. *L. Grünhut. Zeit. phys. Chem. 48, 569 (1904).* — "In dilute aqueous solution, borax decomposes completely into sodium metaborate and free boric acid. If carbon dioxide be passed into the cold solution, sodium bicarbonate is formed and the boric acid of the metaborate is set free. If carbon dioxide and an excess of free boric acid be added, metaborate is formed by mass action, but the amount is small. In mineral waters, which contain free carbon dioxide, the small amounts of boric acid must be present as the free acid,  $H_3BO_3$ ." W. D. B.

The state of hydrogen sulphide in mineral springs. *F. Auerbach. Zeit. phys. Chem. 49, 217 (1904).* — The dissociation constant for hydrogen sulphide

is  $0.91 \times 10^{-7}$  at  $18^\circ$ . From this the author calculates the percentage of free hydrogen sulphide in mineral springs.  
W. D. B.

**The ammonia-soda process as a phase rule study.** *P. F. Fedotieff. Zeit. phys. Chem.* 49, 162 (1904). — The author has made a pretty complete study at  $15^\circ$  of the reaction



in presence of 'aqueous carbonic acid under atmospheric pressure. Some measurements were also made at  $0^\circ$ ,  $30^\circ$  and  $45^\circ$ . If the best utilization of the salt were the sole factor, the author believes that it would be better to add solid salt direct.  
W. D. B.

**The physical chemistry of the lead chamber process.** *M. Trautz. Zeit. phys. Chem.* 47, 513 (1904). — The reactions in the chamber process take place so rapidly that our present methods do not permit us to tell which is the more important. The author has studied the oxidation of sulphur dioxide in aqueous solution in presence of nitrogen compounds; the rate of decomposition of nitrosyl sulphuric acid at  $25^\circ$ ; the equilibria for  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_4$ ,  $\text{HNO}_2$ ,  $\text{HNO}_3$ ,  $(\text{HSNO}_2)$  and  $\text{H}_2\text{SO}_4$  as affected by temperature and concentration of sulphuric acid. The theory of Raschig is considered the most satisfactory, and it is shown that nitric oxide can reduce sulphuric acid to sulphur dioxide in presence of nitric acid. Under conditions prevailing in the chamber process the following reaction can take place:



It is also shown that the present methods for analyzing the gases in the lead chamber are inaccurate. A six-months' sickness is cited as proof of the harmful properties of nitrogen peroxide.  
W. D. B.

**The precipitation of suspensions or colloids and the agglutination of bacteria.** *H. Bechhold. Zeit. phys. Chem.* 48, 385 (1904). — There is no fundamental difference between the precipitation of bacteria, agglutinated bacteria and suspensions or colloids. When the concentrations of the electrolyte and of the colloid are too low, practically no coagulation occurs. When the concentration of the electrolyte is too high, the rate of coagulation is independent of the concentration. For a narrow range just above the lower limit, the rate varies with the concentrations. While the precipitation of unorganized suspensions can be prevented by addition of albumen, gelatine, etc., this is not the case with agglutinated bacteria and is probably not true for bacteria. The precipitation of bacteria and agglutinated bacteria depends on the valency, the migration velocity and the decomposition voltage of the cation, also on the dissociation of the electrolyte.  
W. D. B.

**An attempt to explain agglutination processes.** *W. Biltz. Zeit. phys. Chem.* 48, 615 (1904). — The agglutination process is looked upon as essentially one of adsorption. It is known that some inorganic colloids will precipitate certain other inorganic colloids and it is now shown that a similar precipitation may occur with organic colloids or with bacteria. A very efficient inorganic colloid of this type would practically be an antitoxine.  
W. D. B.

## Velocities

**Inversion of cane sugar caused by platinum metals.** *F. Plzak and B. Husek. Zeit. phys. Chem.* 47, 733 (1904). — The rate of inversion of cane sugar by palladium varies with the preceding history of the palladium. This is probably due to the presence of oxide which partially neutralizes the dilute hydrochloric acid in acid solutions, but which is more effective in neutral solutions than the metal. Platinum is a stronger catalytic agent than palladium, while iridium is weaker. *W. D. B.*

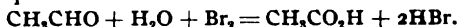
**The kinetics of the sugar inversion.** *J. W. Mellor and L. Bradshaw. Zeit. phys. Chem.* 48, 353 (1904). — It is stated that the reaction velocity constant in the sugar inversion is not really a constant and that the reaction is not as simple as has been assumed. The authors discuss two possibilities: the formation of an acid through the decomposition of invert sugar; and that the dextrose and levulose each show birotation. The first hypothesis does not seem to describe the facts and it has not yet been possible to get data which will establish the second. *W. D. B.*

**Catalysis of ethyl acetate by nitric acid in presence of alkali nitrates.** *H. Lunden. Zeit. phys. Chem.* 49, 188 (1904). — Addition of potassium or sodium nitrate increases the catalytic action of nitric acid on ethyl acetate about 2.3 percent per 0.1 equivalent added. This is only about half the effect which chlorides have on hydrochloric acid. No such difference exists in the inversion of sugar. *W. D. B.*

**Rates of absorption between solids and gases.** *A. Hantzsch. Zeit. phys. Chem.* 48, 289 (1904). — This paper deals with the rate of absorption of gaseous ammonia by finely-divided solid acids and of gaseous hydrochloric acid by solid amines. When pure ammonia is used at constant pressure, the reaction is of the first order because only the surface of the solid acid changes concentration. When the ammonia is diluted with air and is not present in large excess, the reaction is of the second order. A number of experiments have been made and the calculated constants are surprisingly good when one considers the possibility of error. The object of this paper was to show that in this was a difference which can be detected between real acids or bases and pseudo acids or bases. No experiments with the pseudo substances are given in this article. *W. D. B.*

**The rate of crystallization of binary melts.** *F. Dreyer. Zeit. phys. Chem.* 48, 467 (1904). — At bath temperatures corresponding to the falling branch of the rate of crystallization curve, some substances increase the rate of crystallization of formanilide while others decrease it. On the rising branch all substances, so far as tried, decrease the rate of crystallization. *W. D. B.*

**Action of bromine on aqueous acetaldehyde.** *S. Bugarszky. Zeit. phys. Chem.* 48, 63 (1904). — In dilute aqueous solution bromine oxidizes acetaldehyde according to the equation:



The reaction is bimolecular with hydrobromic acid acting as a disturbing factor. The ratio of the reaction velocity constants is 2.55 for a change of  $10^\circ$ . *W. D. B.*

**The reduction of nitro compounds by stannous halides.** *H. Goldschmidt and K. Ingebretsen. Zeit. phys. Chem.* 48, 435 (1904). — The rate of reduction of a nitro compound by stannous chloride and hydrochloric acid is directly proportional to the concentrations of the three reacting substances. This can be explained by assuming that the reaction measured is the reduction of nitro compound to nitroso compound and that the reducing agent is a complex anion  $\text{SnX}_3'$ . Special experiments showed that nitroso compounds do react instantaneously with stannous chloride and hydrochloric acid. The assumption in regard to the complex anion is supported by the fact that stannous bromide and hydrobromic acid reduce nearly eight times as fast as stannous chloride and hydrochloric acid even though the potential difference of the two solutions against platinum is said to be nearly the same. In the case of *o*-nitraniline the reaction velocity increases more rapidly than the increase in hydrochloric acid. This is apparently the result of hydrolysis in the more dilute solutions, the active substance being the substituted ammonium cation. For some unknown reason *p*-nitrophenol gives a very low reaction velocity constant.

W. D. B.

**The catalytic action of metal chlorides.** *H. Goldschmidt and H. Larsen. Zeit. phys. Chem.* 48, 424 (1904). — The rate of action of chlorine on nitrobenzene in presence of stannic chloride or aluminum chloride is proportional to the concentrations of the chlorine and the chloride. The velocity of the reaction between benzyl chloride and anisol in presence of aluminum chloride is proportional to the concentration of the benzyl chloride and the aluminum chloride, the anisol of course being present in large excess.

W. D. B.

**The mathematical expression for the rate of flow through the cell according to the first and third arrangements of Pfeffer.** *W. W. Lepeschkin. Zeit. phys. Chem.* 48, 596 (1904). — The author discusses the conditions for constant flow when a cell is bounded by two semipermeable membranes, one of which can withstand a higher pressure than the other. For the benefit of physical chemists it would have been better to have preceded this paper by one on the possible existence of such membranes. It is very probable that there is no such thing as a semipermeable membrane. If there are such things, it is difficult to find a flaw in van 't Hoff's proof that they must all give the same pressure. If there are no such things, the author's problem is one of relative diffusions only and he has no right to postulate impermeability to the solute.

W. D. B.

#### Electromotive Forces

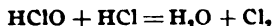
**The effect of pressure on the electromotive force of gas cells.** *T. Wulf. Zeit. phys. Chem.* 48, 87 (1904). — The decomposition voltage of various electrodes was found to be independent of the pressure, while the potential difference of the corresponding gas electrode varied with the pressure according to Helmholtz's formula. From this it is concluded that the potential at which a larger current begins to flow is not the same as that at which gas bubbles appear at the electrode. The difference between the two is slight for sparingly soluble gases such as hydrogen, but greater for soluble gases such as chlorine. With hydrogen the two points are 0.08 volt apart at about 600 atmospheres, while they are 0.05–6 volts apart for chlorine at one atmosphere.

W. D. B.

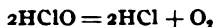
**The theory of capillary electrical phenomena, I.** *J. Billitzer. Zeit. phys. Chem.* 48, 513 (1904). — The author modified Palmer's apparatus by introducing a constant electrode as well as a parasitic one. If the dropping mercury passes through the electrolyte between the parasitic and the constant electrodes, potential differences remain after the flowing electrode has been shut off, which are very different from those while the electrode is flowing and usually have the reverse sign. If the dropping mercury does not pass between the two electrodes, the potential difference does not change the moment the flowing electrode is shut off. There is reason to believe that a current passes while the flowing electrode is working even though the circuit is open. The general result of the investigation is that the absolute potential difference between mercury and the solution is between  $-0.37$  and  $-0.43$  volt, the hydrogen electrode in normal sulphuric acid being taken as zero. This agrees well with the value of  $-0.4$  volt found by method of electrical endosmose. *W. D. B.*

**The theory of capillary electrical phenomena, II.** *J. Billitzer. Zeit. phys. Chem.* 48, 542 (1904). — On expanding or contracting a mercury surface in different electrolytes, differently directed currents are generated. The direction of these currents reverses at two points, at  $+0.35$  volt and  $-0.4$  volt. There is also a current between mercury in a stationary electrolyte and mercury in a moving electrolyte, but this reverses only at  $-0.4$  volt. The author explains why he believes that the reversal at  $+0.35$  volt (Ostwald's zero) does not mark the disappearance of the electrical double layer. *W. D. B.*

**Electromotive behavior of hypochlorous acid.** *W. Nernst and J. Sand. Zeit. phys. Chem.* 48, 601 (1904). — From Jakowkin's experiments on the reaction



the authors calculate the data for the reaction



and thus the potential difference between platinum and a solution of hypochlorous acid. The calculated values agreed with those found experimentally for intermediate concentrations of hypochlorous acid. The agreement was not good for very dilute solutions. *W. D. B.*

**The passivity of metals.** *W. J. Müller. Zeit. phys. Chem.* 48, 577 (1904). — It is assumed that a metal consists of an atom or molecule plus a number of positive and negative electrons. When a metal dissolves as anode it loses the number of negative electrons corresponding to its valency and becomes a positively charged ion. When a metal becomes passive, it loses positive electrons, and changes its valence. It is therefore believed that all metals having two or more valences can become passive under suitable conditions, and that a non-metallic layer is not the cause of passivity. From the analogy between iron and chromium, it is assumed that passive iron is hexavalent. No proof is offered for any of the views advanced. *W. D. B.*

#### *Electrolysis and Electrolytic Dissociation*

**The passivity of nickel.** *M. Le Blanc and M. G. Levi. Boltzmann's Festschrift*, 183 (1904). — Nickel dissolves quantitatively as anode in halide,

cyanide and sulphuric acid solutions. In chlorate, nitrate, sulphate, carbonate and potassium hydroxide solutions, practically no nickel dissolves. In acetate solutions the electrode loss varies with the previous history of the anode. At a temperature of 80°, nickel dissolves readily in everything except potassium hydroxide solution. Increasing the current density decreases the current efficiency. With a sodium sulphate solution, changing the concentration had no effect. A number of experiments were also made with mixed electrolytes. Traces of a halide were enough to make the nickel dissolve quantitatively.

W. D. B.

**The anodic behavior of copper and aluminum.** *F. Fischer. Zeit. phys. Chem.* 48, 177; *Zeit. Elektrochemie*, 10, 543 (1904).—With a high current density a copper anode in sulphuric acid becomes coated with a mixture of cuprous and cupric sulphate, the ratio of the former to the latter increasing with rising temperature. At the boiling-point this crust is blown off and the cuprous sulphate decomposes to metallic copper and cupric sulphate. At this temperature half the copper dissolves as cuprous salt. The breaking down of the film on copper or aluminum anodes can be prevented by cooling the anodes. The oxygen polarization at an aluminum anode in sulphuric acid is said to be of the same order as at a platinum anode. The cutting down of the current is believed to be due to the resistance of the film. When the current is reversed, the hydrogen ruptures the film and the current passes through readily. The weak point here is that this calls for a continuous corrosion of the aluminum anode, and it is very doubtful whether this occurs. A preliminary account of this work has already been published (8, 73).

W. D. B.

**The electrolytic oxidation of sodium thiosulphate.** *C. J. Thatcher. Zeit. phys. Chem.* 47, 641 (1904).—In neutral or slightly alkaline solutions sodium thiosulphate is oxidized to tetrathionate, no other reaction taking place when platinized electrodes are used. The presence of mercuric cyanide or brucine prevents the oxidation. It seems probable therefore that the reaction  $S_2O_3^{2-} \rightarrow S_4O_6^{2-}$  is an indirect one. The formation of sulphur, sulphite or sulphate takes place only in acid or in strongly alkaline solutions and is always due to a secondary reaction. In alkaline solution, tetrathionate hydrolyzes to thiosulphate and trithionate.

W. D. B.

**The strength of hypochlorous acid.** *J. Sand. Zeit. phys. Chem.* 48, 610 (1904).—The conductivity of hypochlorous acid cannot be measured directly owing to decomposition. An indirect method was adopted. If different solutions are saturated at atmospheric pressure with carbon dioxide, it is assumed that the concentration of undissociated carbon dioxide will be the same in all the solutions. [This is necessarily true only in case the solutions are non-miscible.] For measurements of the absorption coefficient of carbon dioxide and from calculations of the concentration of bicarbonate as ion, etc., the author deduces a dissociation constant at 17° for hypochlorous acid of  $3.7 \times 10^{-8}$ .

W. D. B.

**The determination of the solubility of salts of weak acids from the conductivity.** *D. Gardner and D. Gerassimoff. Zeit. phys. Chem.* 48, 359 (1904).—

It was believed that Kohlrausch's data for the solubility of barium carbonate were vitiated by hydrolysis. The conductivity was therefore measured in solutions of caustic soda. As the concentration of the caustic increased, the conductivity due to the barium carbonate decreased. By extrapolation the conductivity of barium carbonate with no hydrolysis is estimated to be  $6.0 \times 10^{-6}$  at  $18^\circ$ .  
W. D. B.

**The theory of pseudo acids.** *H. Kauffmann. Zeit. phys. Chem.* 47, 618 (1904). — It has been shown by Hantzsch that the sodium salts of pseudo acids show a lesser degree of hydrolysis than would be expected from the dissociation of the free acid. The author calculates that this is not in accord with the conclusions to be drawn from an application of the mass law. Since the fact is well established, the author decides that some unknown source of error exists which has thrown his calculations out.  
W. D. B.

**Electrical conductivity of solutions in bromine.** *W. A. Plotnikow. Zeit. phys. Chem.* 48, 220 (1904). — Concentrated solutions of phosphorus pentabromide in bromine conduct well; solutions of  $\text{AlBr}_3$ ,  $\text{CS}_2$  and  $\text{AlBr}_3 \cdot \text{C}_2\text{H}_5$ ,  $\text{BrCS}_2$  fairly well; solutions of  $\text{SbBr}_3$  only slightly; while solutions of  $\text{AlBr}_3$ ,  $\text{SbBr}_3$ ,  $\text{AsBr}_3$  and  $\text{SnBr}_4$  do not conduct. The author believes that the conductivity of a solution depends on the properties of the solvent and the nature of the solute, meaning thereby that chemical compounds are formed.  
W. D. B.

**Physical-chemical investigations of the amide group.** *C. E. Fawsitt. Zeit. phys. Chem.* 48, 585 (1904). — Contrary to the statement of Rudorf, carbamide does not decrease the viscosity of water. Addition of urea to solutions of potassium chloride and sodium hydroxide changes the conductivity in a different way from addition to hydrochloric acid. Urea is a very weak base with no acid properties at all.  
W. D. B.

#### Dielectricity and Optics

**Determination of the dielectric constant of ice in liquid air by Drude's method of rapid oscillations.** *U. Behn and F. Kiebitz. Boltzmann's Festschrift*, 610 (1904). — At  $-190^\circ$  the dielectric constant for ice lies between 1.76 and 1.88, while the electromagnetic theory of light calls for a value of 1.74 to 1.77. Pure ice has about the same dielectric constant at  $-2^\circ$  as at  $-180^\circ$ . The same is true of ice from ordinary distilled water provided the water be frozen rapidly. If the water is frozen slowly a network of channels is probably formed and the dielectric constant is much higher.  
W. D. B.

**Temperature determinations on radiating gases.** *H. Kayser. Boltzmann's Festschrift*, 38 (1904). — When the temperature of a solid is raised, the emission spectrum extends further into the ultra-violet. Experiments on the  $\text{H}_\alpha$ ,  $\text{H}_\beta$  and  $\text{H}_\gamma$  lines show that the relative intensities of the shorter waves increase with increasing current and decreasing pressure. Assuming Wien's law the calculated temperatures for three current strengths and a pressure of 1.2 mm were  $2200^\circ$ ,  $2340^\circ$  and  $2760^\circ$  abs. As these temperatures are not impossible ones, the author believes that it is probable that radiation law for gases resembles qualitatively that for solids.  
W. D. B.

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==THE==  
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**Freezing-point, Boiling-point and Conductivity Methods**

By Harry C. Jones, Instructor in Physical Chemistry in Johns Hopkins University.

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# MOLECULAR ATTRACTION

(THIRD PAPER)

BY J. E. MILLS

In a preceding paper,<sup>1</sup> making use of the measurements of Profs. Ramsay and Young and of Prof. Young, we applied the theoretically derived equation,

$$(1) \quad \frac{L - E_1}{\rho^3 d - \rho^3 D} = \text{constant},$$

to twenty-one substances, and called particular attention to variations in the constants obtained and to the range of temperature covered by the measurements. (In the above equation,  $L$  denotes latent heat of vaporization,  $E_1$  is energy spent in overcoming external pressure, and  $d$  and  $D$  denote density of liquid and vapor respectively.) In this paper, making use of the same measurements and the results there derived, we wish to point out some further applications of the theory. But first we call attention to several points bearing more directly upon the results of the last paper.

The constant given by equation 1 above, as will appear later in this article, is an important property of a substance and depends upon the attraction of one molecule for another. We have to refer to this constant so often that a more specific designation is desirable. We have hitherto called the absolute attraction at unit distance from a molecule  $\mu$ . The above constant we will call  $\mu'$ . (Therefore  $\mu = c\mu' \rho^3 m$ .) We call the internal latent heat of vaporization  $\lambda$ , and therefore have,

$$(2) \quad \lambda = \mu'(\rho^3 d - \rho^3 D).$$

**The  $\frac{\partial P}{\partial T}$  at the Critical Temperature**

In the second paper we commented upon the difficulty of

<sup>1</sup> Jour. Phys. Chem. June, 1904. Referred to in this article as "Second Paper."

obtaining correctly the  $\frac{\partial P}{\partial T}$  from Biot's formula near the critical temperature. We entirely overlooked the fact that the constant  $b$  of the equation,  $p = bT - a$ , proposed by Profs. Ramsay and Young, was also a  $\frac{\partial P}{\partial T}$ , and that at the critical temperature (but only at that point, see p. 623), the  $\frac{\partial P}{\partial T}$  of the two equations became identical. In work done to establish the truth of the equation,  $p = bT - a$ , the  $\frac{\partial P}{\partial T}$  was obtained for three substances at volumes practically identical with the critical volume. The results are such as to confirm entirely and quantitatively the view that the divergences at this point in  $\mu'$  were due to the Biot formula used to obtain the  $\frac{\partial P}{\partial T}$ .

Thus isopentane gives at the critical temperature (volume 4.266) the  $\frac{\partial P}{\partial T} = 367.8$ , calculated from Biot's formula. Prof. Young<sup>1</sup> found from drawn isochors (at the volume 4.3) the value 397 and a calculated value of 407. Therefore Biot's formula gives results about ten percent too low, an amount just sufficient to explain the variation in  $\mu'$  near that point.

For normal pentane, Biot's formula at the critical volume, 4.303, gives 364.8 for the  $\frac{\partial P}{\partial T}$ . Mr. J. Rose-Innes and Dr. Young<sup>2</sup> obtained 407.3 from drawn isochors. Biot's formula therefore shows results too low by about eleven percent, an amount which is sufficient to explain the low values obtained in the constant  $\mu'$  as the critical temperature was approached.

For ethyl oxide Profs. Ramsay and Young<sup>3</sup> obtained at volume 4.00 the  $\frac{\partial P}{\partial T} = 413.7$ , and it is evident from their paper on ethyl oxide<sup>4</sup> that the values they used for calculating the

<sup>1</sup> Proc. Phys. Soc. 1894-95, p. 650.

<sup>2</sup> Phil. Mag. April, 1899.

<sup>3</sup> Ibid. May, 1887.

<sup>4</sup> Phil. Trans. 1887A, p. 57.

latent heat of vaporization point to a value at this point of about 490, a fact which sufficiently explains the rise noted in the value of  $\mu'$ . (The values Profs. Ramsay and Young used for  $\frac{\partial P}{\partial T}$  at this point are not in accord with the Biot formula they published, which prevents quantitative comparison here. See p. 635.)

We have therefore direct proof that the equation,

$$\frac{L - E_1}{P^2 d - P^2 D} = \text{constant},$$

is applicable in the immediate neighborhood of the critical temperature.

#### The Product of the Pressure and the Vapor Density

In examining the data used to discover if possible the immediate source of variations in  $\mu'$  it proved impracticable to plot either the pressure or the volume of the vapor directly against the temperature. But their product,  $PV$ , varied more slowly and the values were plotted and gave regular curves except for di-isobutyl, brom-benzene, iodo-benzene, hexamethylene, and water. This result is so interesting that the curves are given below, Diagrams 1 to 3. The numerical results are given in Tables 1 to 21. For water the break in the regularity of the curve occurs at  $100^\circ \text{C}$ , and since different formulas were used for the vapor pressure above and below that temperature it would seem certain, in view of remarks already quoted (Second paper, p. 396), that the formulas for the pressure need adjustment. For di-isobutyl, brom-benzene, iodo-benzene, and hexamethylene, the irregularities of the  $PV$  curve are more probably due to the vapor density (See second paper, p. 400), and are especially interesting because they occur at just the point where were obtained divergent values for  $\mu'$ . Reference to the preceding paper will show that di-isobutyl, brom-benzene, and iodo-benzene, were the only substances, except stannic chloride and the associated substances, giving divergences (which have not been explained as due to multiplication of the error in calculating the  $\frac{\partial P}{\partial T}$ ) greater than two percent from the mean value



adopted for  $\mu'$ . Hexamethylene shows likewise a smaller

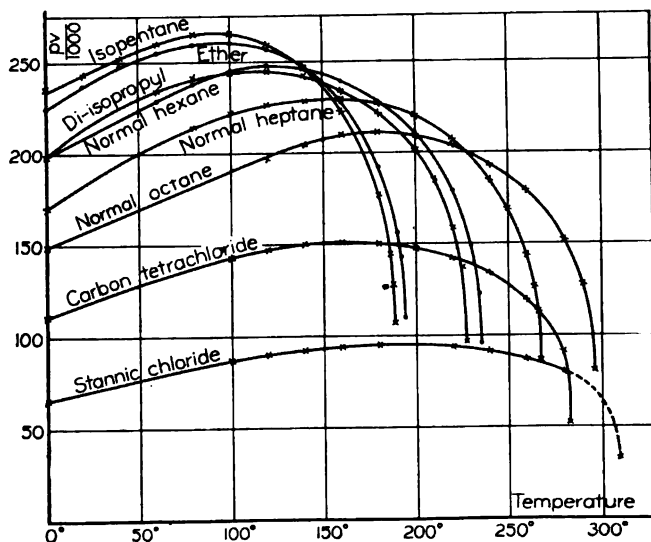


Diagram 1

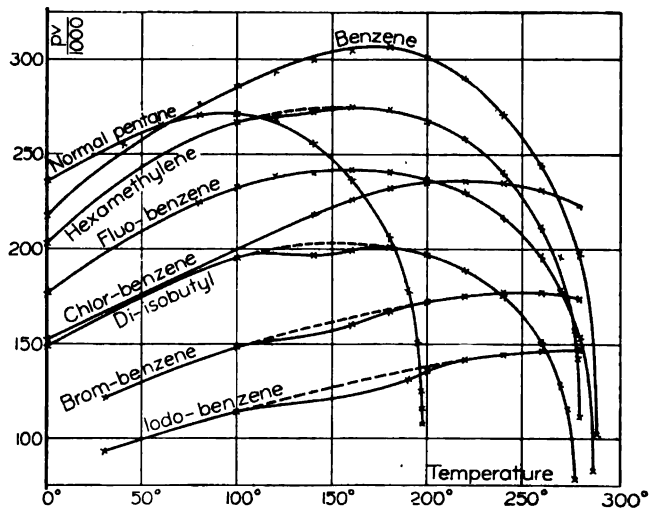


Diagram 2

though well marked divergence in  $\mu'$  corresponding to the concave sink in the PV curve.

It is clear therefore that these abnormal values of the PV product must be carefully investigated before the corresponding divergences in  $\mu'$  can be regarded as in anyway evidence against the theory by which that constant is derived.

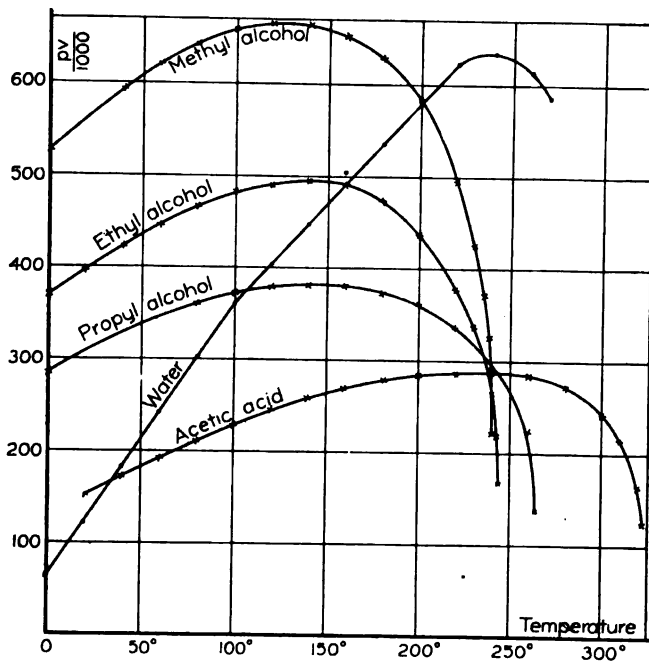


Diagram 3

For water, add 900 to the ordinates shown by the diagram

### Internal Heat of Vaporization

The internal heat of vaporization was plotted against the temperature, Diagrams 8 to 10. These curves are more fully discussed later (p. 618). We would here call attention only to one feature of these curves, viz: Corresponding to divergences in  $\mu'$  there appear irregularities in these curves and these variations in  $\mu'$  would (excepting in stannic chloride and the associated substances) for the most part disappear if the curves were smoothed and the smoothed values thus obtained used in the calculations.

Diagram of  $L - E_1$  against the  $\rho'd - \rho'D$

We have plotted, Diagrams 4 to 7, the results for all of the substances examined, using the values of  $L - E_1$  for ordinates and the values of  $\rho'd - \rho'D$  for abscissæ. This is desirable in order to give a more exact idea of the relative ex-

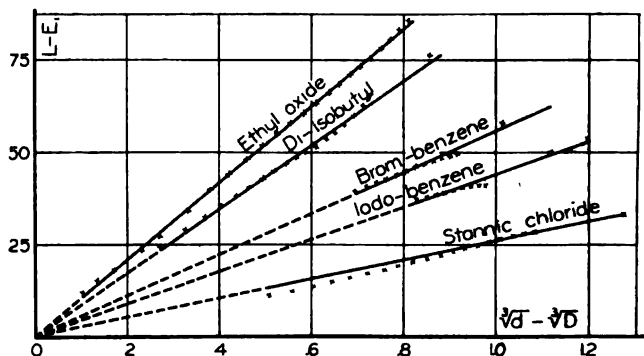


Diagram 4

Ordinates give internal heat of vaporization in calories. Abscissæ give difference of the cube roots of the densities of liquid and vapor

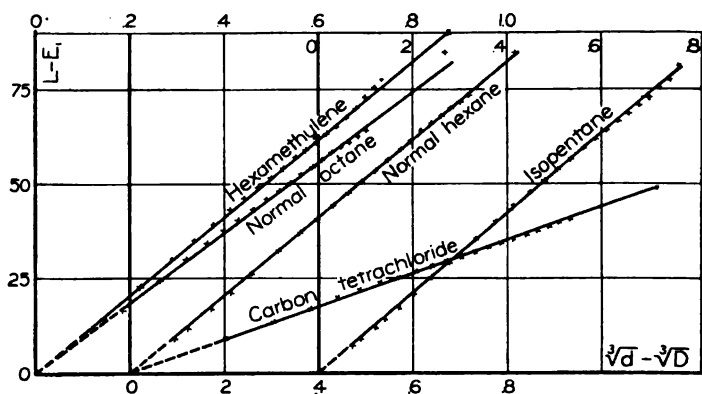


Diagram 5

Ordinates give internal heat of vaporization in calories. Abscissæ give difference of the cube roots of the densities of liquid and vapor

tent and importance of the observations. For since neither  $L - E_1$  nor  $\rho'd - \rho'D$  vary uniformly with the temperature observations taken every ten degrees are consequently not taken

at equal intervals of the curve (a straight line) represented by that equation.

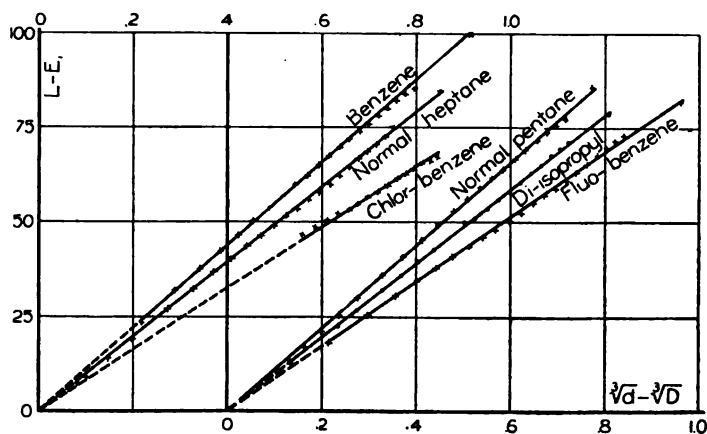


Diagram 6

Ordinates give internal heat of vaporization in calories. Abscissæ give difference of the cube roots of the densities of liquid and vapor

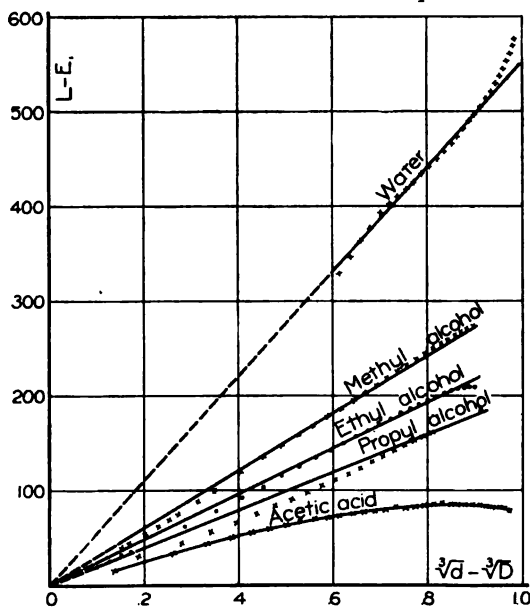


Diagram 7

Ordinates give internal heat of vaporization in calories. Abscissæ give difference of the cube roots of the densities of liquid and vapor

Through each set of observations, excepting for acetic acid, the mean line is drawn. The constants for this mean line were obtained by averaging, for any substance, all of the constants recorded in Table 1 (Second paper) that were within two per cent of the mean values adopted in that table. For di-isobutyl the mean value adopted appeared probably too high and we therefore choose the value 86.3 as being more nearly in accord with the proper constant. The values for these constants are given in Table 25 under the heading  $\mu'$ .

For ethyl oxide, di-isopropyl, di-isobutyl, isopentane, normal pentane, normal hexane, normal heptane, normal octane, benzene, hexamethylene, fluo-benzene, carbon tetrachloride, methyl alcohol, ethyl alcohol, propyl alcohol, and acetic acid, sixteen substances in all, the observations are practically complete, extending from near the freezing-point of the liquid nearly to the critical temperature. Among these sixteen substances the only divergences appearing marked to the eye are normal octane and ethyl alcohol at  $0^{\circ}\text{C}$ , di-isobutyl, those for the alcohols as the lines approach the origin, and acetic acid.

The curves for chlor-benzene, brom-benzene, iodo-benzene, stannic chloride, and water, are not complete. All of these incomplete curves show irregularities and yet it is made most evident by the diagrams, as well as by what has already been said, that with the exception of stannic chloride, the divergences are not so pronounced as to be considered weighty evidence against the theory.

In conclusion therefore we point out that, of the twenty-one substances examined, stannic chloride and the associated substances (methyl alcohol, ethyl alcohol, propyl alcohol, and acetic acid), are the only substances that show variation in  $\mu'$  without at the same temperature exhibiting irregularities in the data used. That these irregularities in the data are due to the measurements is much to be doubted. But if not so produced, they are significant of unknown changes taking place in the substance under examination — changes which were not taken into account in the theory of molecular attraction under discus-

sion and to which that theory as outlined would not be strictly applicable.

### The Latent Heat of Vaporization

It is interesting to examine more closely and to compare the heats of vaporization calculated by use of the following equations :

$$(3) \quad L = \int T (V - v) \frac{\partial P}{\partial T}.$$

$$(4) \quad L = \mu'(\bar{v}^2 d - \bar{v}^2 D) + E_1.$$

$$(5) \quad L = 2RT \log e \frac{d}{D}.$$

Using the constants we have hitherto adopted, the equations become :

$$(6) \quad L = 0.031833 T(V - v) \frac{\partial P}{\partial T} \text{ cal.}$$

$$(7) \quad L = \mu'(\bar{v}^2 d - \bar{v}^2 D) + 0.031833 P(V - v) \text{ cal.}$$

$$(8) \quad L = \frac{9.1522}{m} T \log \frac{d}{D} \text{ cal.,}$$

$m$  being the molecular weight, with oxygen equal to 16 as the standard, and logarithms to base ten.

The equations are all theoretically derived.

Equation 3 rests primarily upon the first and second laws of thermodynamics and is deduced therefrom by a familiar line of reasoning. No assumption is made as to the nature or cause of the latent heat, or as to the nature of the substance itself. The equation will serve as well to calculate the latent heat of fusion or the energy absorbed during the change in the crystalline form of a solid. It merely expresses the energy necessary to effect a change in volume under given conditions, and is silent as to the cause of the change or the nature of the substance. So far as present knowledge goes there is no need for questioning the correctness of the results obtained by this equation, the data being accurate. We can therefore well use the latent heat so obtained as a check, either upon direct measurements of the latent heat, or upon other calculations involving relations and assumptions which perhaps are true, but which are not so fundamental.

We have already published (Second paper, Tables 2 to 22 the calculations for six or seven of the substances were, however, the work of others), the results obtained by the application of this equation to twenty-one substances, and only for the sake of comparison repeat a portion of the results in the tables which follow. (See Tables 1 to 21, under the head Ther.) It must be borne in mind that although these results are accurate where the data is correct, yet errors in the measurements may, and oftentimes certainly do (because of the method necessarily followed for obtaining the  $\frac{\partial P}{\partial T}$ ), produce far greater proportional errors in the result.

Equation 4 is derived by a simple transposition from equation 2 of the second paper. The assumptions upon which that equation is founded and evidence bearing upon the equation, have been discussed in the preceding paper, and here we would only summarize by saying that the equation rests upon the belief that the total kinetic energy of a molecule of a liquid and of its vapor, at the same temperature are the same; and upon the further assumption that the entire latent heat of vaporization is expended in overcoming the external pressure and in separating the molecules against the action of an attractive force varying inversely as the square of the distance apart of the molecules. The equation is not applicable (*a priori*) if (a) the number of molecules change owing to dissociation or decomposition; or if (b) the molecules are not evenly distributed throughout the space occupied by them; or if (c) for any reason the attraction between these molecules varied with the temperature.

The constants  $\mu'$  for the twenty-one substances examined are given in Table 25 of this article under the heading  $\mu'$ , and while the constants there given were obtained by a comparison of this equation with the thermodynamical results obtained by use of equation 3, it is easily seen that such a method of obtaining the constant is, we might say, incidental, and only adopted for the sake of accuracy and convenience. One accurate measurement at *any* temperature of the latent heat of vaporization of any substance to which the equation is applicable, together with

a measurement of its vapor pressure and of the densities of liquid and vapor, would enable the constant for that substance to be calculated. The equation, has, therefore, no connection with the thermodynamical equation 3, but rests independently, partly upon the same and partly upon additional assumptions.

The results obtained for the twenty-one substances are given below, Tables I to 21, in the columns marked Mills.

In comparing the latent heats so calculated with those obtained from the thermodynamical equation we find that if the five associated substances be omitted, there are only four determinations in which the results as calculated by the two equations differ by so much as two calories, viz: di-isobutyl at  $0^{\circ}$ , normal octane at  $0^{\circ}$ , chlor-benzene at  $270^{\circ}$ , and brom-benzene at  $30^{\circ}$  — in every instance the divergences being at the end-point of the Biot curve and thus making it probable that all of these divergences are due to the thermodynamical equation. Excepting stannic chloride, there are only twelve other instances in which the divergence is greater than one calorie. All of these divergences are marked with an asterisk in the tables.

TABLE I  
Ethyl Oxide

Temperature	Heat of vaporization			
	Ther.	Mills	Crompton	PV/1000
0	93.27	91.59*	99.42	224
20	87.90	87.94	93.42	237
40	83.18	83.85	87.62	247
60	78.84	79.46	81.95	255
80	73.95	74.49	76.03	259
100	68.35	68.89	69.76	260
120	62.63	62.41	62.79	256
140	55.52	55.05	55.04	247
160	45.99	45.98	45.71	228
180	31.58	32.54	32.19	192
190	20.90	20.58	20.25	156
192	17.10	16.11	15.84	143
193	13.67	12.61*	12.36	132
194	—	—	—	110



This comparison emphasizes more clearly than is possible in any other way the correctness of the law of molecular attraction we have assumed.

TABLE 2  
Di-isopropyl

Temperature	Heat of vaporization			PV/1000
	Ther.	Mills	Crompton	
0	85.11	85.40	94.24	198
60	76.90	76.42	79.91	234
80	72.86	72.66	75.13	241
100	68.28	68.45	70.15	243
120	63.57	63.85	64.98	244
140	58.58	*58.75	59.46	242
160	52.70	52.87	53.23	234
180	45.86	45.90	45.99	221
200	37.15	37.16	37.05	201
210	31.09	31.31	31.16	185
220	22.14	22.79	22.59	159
225	14.57	15.40	15.23	137
227.35				96.8

TABLE 3  
Di-isobutyl

Temperature	Heat of vaporization			PV/1000
	Ther.	Mills	Crompton	
0	80.99	78.62*	91.35	149
100	69.25	67.52*	69.46	196
120	63.79	64.15	64.99	195
140	59.84	60.70	60.78	197
160	56.30	57.01	56.57	199
180	53.05	53.10	52.28	201
200	48.83	48.51	47.43	197
220	43.80	43.09	41.85	189
240	37.37	36.39	35.08	175
260	27.93	27.08	25.88	151
270	19.54	19.29	18.33	128
274	14.24	14.22	13.46	115
276.8				78.8

TABLE 4  
Isopentane

Temperature	Heat of vaporization			
	Ther.	Mills	Crompton	PV/1000
0	88.86	87.45*	95.92	236
20	82.91	83.52	89.98	243
40	78.69	79.44	84.46	252
60	74.56	75.00	78.96	260
80	70.00	70.12	73.26	265
100	64.78	64.56	67.09	265
120	58.62	58.19	60.16	259
140	51.07	50.52	52.00	246
160	41.27	40.83	41.84	223
180	24.65	25.05	25.54	177
185	16.47	17.17	17.46	153
187	10.43	11.08	11.25	135
187.4	8.07	8.69	8.81	128
187.8	—	—	—	107

TABLE 5  
Normal Pentane

Temperature	Heat of vaporization			
	Ther.	Mills	Crompton	PV/1000
0	93.36	92.38	101.18	236
40	83.63	84.58	89.47	255
60	80.04	80.29	83.98	266
80	75.30	75.39	78.18	271
100	69.87	69.88	71.90	271
120	64.48	63.85	65.34	269
140	56.58	56.31	57.30	256
160	47.42	47.27	47.89	237
180	35.01	35.16	35.43	207
190	24.68	25.38	25.49	178
195	15.66	16.60	16.63	151
197	6.55	7.15	7.14	125
197.15	3.11	3.41	3.41	116
197.2	—	—	—	108

TABLE 6  
Normal Hexane

Temperature	Heat of vaporization			
	Ther.	Mills	Crompton	PV/1000
0	90.98	90.33	100.82	198
60	80.82	81.09	84.86	228
80	77.55	77.43	79.90	238
100	73.65	73.37	74.84	244
120	69.38	68.91	69.67	248
140	63.96	63.75	63.98	247
160	57.63	57.78	57.61	239
180	50.93	51.04	50.59	228
200	42.75	42.78	42.16	211
220	30.37	30.82	30.18	179
230	19.73	20.56	20.04	149
234	10.44	11.26	10.94	123
234.8				95.7

TABLE 7  
Normal Heptane

Temperature	Heat of vaporization			
	Ther.	Mills	Crompton	PV/1000
0	89.86	89.10	100.25	170
80	79.52	79.06	80.66	214
100	75.96	75.76	76.12	222
120	71.79	72.06	71.47	226
140	67.19	67.94	66.69	228
160	62.74	63.47	61.73	229
180	58.52	58.63	56.63	227
200	53.17	52.98	50.83	220
220	46.46	46.09	43.92	207
240	37.45	37.12	35.11	185
260	21.90	22.33	20.90	144
264	15.84	16.48	15.38	127
266.5	8.50	9.15	8.52	107
266.9				87.0

TABLE 8.  
Normal Octane

Temperature	Heat of vaporization			PV/1000
	Ther.	Mills	Crompton	
0	89.46	85.55*	99.98	149
120	70.27	71.55*	71.58	197
140	67.56	68.38	67.52	204
160	64.82	64.96	63.45	210
180	60.99	61.07	59.06	211
200	56.87	56.71	54.38	210
220	52.03	51.72	49.20	204
240	45.97	45.65	43.10	193
260	39.14	38.57	36.15	179
280	28.26	28.13	26.12	152
290	19.10	19.47	17.97	128
296.2				80.5

TABLE 9  
Benzene

Temperature	Heat of vaporization			PV/1000
	Ther.	Mills	Crompton	
0	107.05	107.25	123.89	218
80	94.40	95.75*	102.49	277
100	91.05	92.07*	97.44	286
120	87.36	88.00	92.32	293
140	83.48	83.72	87.27	300
160	79.20	79.18	82.09	305
180	74.53	74.24	76.69	307
200	69.01	68.45	70.43	301
220	62.32	61.74	63.34	290
240	54.21	53.74	54.96	271
260	43.76	43.57	44.40	244
280	27.43	27.79	28.17	197
288.5				102.5

TABLE 10  
Hexamethylene

Temperature	Heat of vaporization			
	Ther.	Mills	Crompton	PV/1000
0	96.22	97.13	111.80	203
100	83.71	82.82	87.47	267
120	78.69	78.89	82.58	270
140	73.60	74.56	77.53	272
160	69.68	70.19	72.61	275
180	65.15	65.27	67.25	274
200	59.37	59.60	61.21	267
220	53.56	53.27	54.56	258
240	45.76	45.37	46.31	240
260	35.16	34.84	35.42	211
270	26.72	26.76	27.14	196
277	16.85	17.34	17.53	157
279	11.78	12.34	12.45	142
279.95	—	—	—	111

TABLE 11  
Fluo-benzene

Temperature	Heat of vaporization			
	Ther.	Mills	Crompton	PV/1000
0	87.39	88.36	102.66	177
80	80.06	79.05	84.62	224
100	77.09	76.06*	80.38	233
120	73.21	72.68	76.02	239
140	68.50	68.91	71.46	240
160	64.37	64.96	66.92	242
180	60.09	60.65	62.17	241
200	55.24	55.76	56.89	236
220	50.28	50.32	51.18	230
240	44.03	43.78	44.34	216
260	35.74	35.30	35.59	196
280	20.95	21.15	21.18	153
286.55	—	—	—	82.6

TABLE 12  
Chlor-benzene

Temperature	Heat of vaporization			PV/1000
	Ther.	Mills	Crompton	
0	87.72	87.25	107.14	152
140	73.37	74.12	79.06	218
160	71.26	71.56	75.63	226
180	68.77	68.75	72.08	232
200	65.65	65.58	68.34	235
220	62.60	62.18	64.46	236
240	59.65	58.48*	60.30	235
260	56.06	54.24*	55.66	231
270	53.95	51.88*	53.10	—
280	—	—	—	223
360.7	—	—	—	81.3

TABLE 13  
Brom-benzene

Temperature	Heat of vaporization			PV/1000
	Ther.	Mills	Crompton	
30	68.68	65.78*	79.45	121
100	62.58	61.77	68.76	148
160	54.69	56.55*	60.39	160
180	53.80	54.80	58.02	167
200	52.27	52.82	55.47	172
220	50.41	50.61	52.80	175
240	48.29	48.24	50.02	176
260	46.30	45.72	47.18	177
270	45.03	44.32	45.62	—
280	—	—	—	174
397.0	—	—	—	59.5

TABLE 14  
Iodo-benzene

Temperature	Heat of vaporization			PV/1000
	Ther.	Mills	Crompton	
30	56.70	55.99	68.77	92.8
100	53.68	53.32	60.08	114
200	45.34	47.01*	49.36	135
220	44.94	45.64	47.57	142
240	43.70	44.02	45.54	144
260	42.50	42.25	43.45	146
270	41.85	41.27	42.31	—
280	—	—	—	147
448	—	—	—	49.7

TABLE 15  
Carbon Tetrachloride

Temperature	Heat of vaporization			PV/1000
	Ther.	Mills	Crompton	
0	51.87	52.50	60.72	111
100	44.20	44.67	47.62	143
120	42.24	42.64	45.13	147
140	40.26	40.51	42.61	150
160	37.95	38.15	39.96	151
180	35.40	35.53	37.08	150
200	32.61	32.58	33.92	147
220	29.45	29.19	30.31	142
240	25.56	25.15	26.05	134
260	20.07	19.73	20.36	119
280	10.43	10.47	10.75	91.2
283.15	—	—	—	52.3

TABLE 16  
Stannic Chloride

Temperature	Heat of vaporization			PV/1000
	Ther.	Mills	Crompton	
0	35.38	35.18	42.19	65.4
100	31.40	30.95	33.29	86.5
120	30.02	29.81	31.67	89.7
140	28.52	28.56	30.02	92.3
160	26.86	27.19	28.38	94.1
180	24.89	25.69	26.66	94.7
200	22.97	24.08*	24.90	94.8
220	20.89	22.28*	22.99	93.9
240	18.60	20.25*	20.88	91.5
260	16.03	17.89*	18.46	87.1
280	13.08	15.06*	15.52	80.3
318.7				32.6

TABLE 17  
Water

Temperature	Heat of vaporization			PV/1000
	Ther.	Mills	Crompton	
0	606.5	574.6	738.4	965
20	592.6	571.2	709.8	1022
40	578.6	565.8	682.4	1082
60	564.7	558.4	656.0	1142
80	550.6	549.4	630.6	1202
100	536.5	538.9	606.5	1260
120	522.3	526.4	582.7	1304
140	508.0	512.8	559.4	1347
160	493.6	498.1	536.4	1404
180	479.0	481.3	513.3	1435
200	464.3	463.8	490.7	1478
220	449.4	445.2	467.4	1523
240	423.8	423.5	442.1	1533
260	394.0	399.3	414.2	1514
270	374.5	385.4	398.5	1486
364.3				345



TABLE 18  
Methyl Alcohol

Heat of vaporization				
Temperature	Ther.	Mills	Crompton	PV/1000
0	289.2	289.4	324.4	527
20	284.5	283.1	307.2	561
40	277.8	275.8	290.3	593
60	269.4	266.9	273.6	621
80	259.0	256.8	256.9	643
100	246.0	245.1	240.0	658
120	232.0	231.7	222.7	665
140	216.1	216.6	205.0	664
160	198.3	199.4	185.8	652
180	177.2	179.3	164.9	629
200	151.8	154.4	140.0	585
220	112.5	118.5	106.2	494
230	84.5	92.2	81.9	426
236	61.7	68.9	61.0	372
238.5	44.2	51.1	45.0	326
240	—	—	—	220

TABLE 19  
Ethyl Alcohol

Heat of vaporization				
Temperature	Ther.	Mills	Crompton	PV/1000
0	220.9	228.4	238.0	369
20	220.6	223.9	224.3	396
40	218.7	218.3	210.8	423
60	213.4	211.4	197.5	446
80	206.4	203.4	184.2	467
100	197.1	194.4	171.2	483
120	184.2	183.6	157.9	490
140	171.1	171.2	144.5	494
160	156.9	157.7	130.7	491
180	139.2	141.7	115.6	474
200	116.6	121.7	97.8	437
220	88.2	94.6	74.8	377
240	40.3	45.8	35.5	265
242.5	22.1	26.5	20.3	219
243.6	—	—	—	167

TABLE 20  
Propyl Alcohol

Temperature	Heat of vaporization			PV/1000
	Ther.	Mills	Crompton	
0	194.4	190.8	200.9	284
80	173.0	172.4	153.7	360
100	164.0	165.2	142.7	373
120	153.0	157.0	132.0	379
140	142.4	147.9	121.5	381
160	129.0	137.6	110.7	381
180	116.3	125.8	99.9	373
200	102.2	112.7	88.2	362
220	85.3	96.6	74.7	336
240	63.4	75.3	57.5	290
260	33.5	41.4	31.2	224
263.7	—	—	—	137

TABLE 21  
Acetic Acid

Temperature	Heat of vaporization			PV/1000
	Ther.	Mills	Crompton	
20	84.05	—	184.80	153
40	87.02	—	176.94	173
60	89.69	—	169.46	192
80	91.59	—	162.05	211
100	92.32	—	154.62	228
120	94.38	—	147.20	246
140	91.83	—	139.58	259
160	89.63	—	131.82	269
180	87.71	—	123.95	278
200	85.55	—	115.73	284
220	82.02	—	106.72	286
240	78.18	—	97.21	288
260	72.26	—	86.44	284
280	63.39	—	73.61	272
300	48.95	—	56.86	243
310	37.77	—	44.37	216
320	18.04	—	22.67	164
321.65	—	—	—	124

Accurate calorimetric measurements are exceedingly difficult even under ordinary pressures, and it is not too much to say that where equation 4 is applicable, latent heats calculated with its aid will be more accurate than direct measurements of that quantity, unless very great care is taken in the measurements.

Equations 3 and 4 give with the associated substances and with stannic chloride an agreement which is partial but not complete, divergences being shown at the higher temperatures. One or more of the modifying causes mentioned on page 602 may here be operative.

Equation 5 was deduced by Mr. H. Crompton. Mr. Crompton considers the change in density as if it were due to pressure alone, then in order to keep the substance at that density without the excess of pressure doubles the amount of energy required. Thus he has,

$$(9) \quad L = 2 \int_v^v p \partial v = 2RT \log_e \frac{d}{D}.$$

Mr. Crompton makes no supposition as to the true cause of the change of density. But he proceeds on the principle that in effecting a given change of condition the process pursued is immaterial if the total energy change is alone to be considered, the idea being that the change in density could, theoretically, have been produced by pressure. The law governing the change of pressure with the density is known, therefore the amount of energy involved in the change of state can be calculated.

Mr. Crompton uses as the law governing the change of pressure with the volume, the gas equation,  $PV = RT$ . But since Mr. Crompton deals with an ideal condition, from which the action of forces other than the pressure are by assumption removed, his equation is not limited to those temperatures for which that equation holds true. It is necessary, however, that  $PV = RT$  should represent the true law of pressure for the substance, which is ideally considered only in a limited sense. (The material size of the molecules or some effect of the temperature, etc., *might*, therefore, affect the exactness of the law.)

It will be further recognized that Mr. Crompton's equation, no less than equation 4 above, involves the assumption that the only energy change is that involved in a change in density — that is, a change of potential energy, — and the total kinetic energy of the molecules of the liquid and of the gas must be the same. As a consequence it is to be expected, though not with certainty, owing to possible compensation, that the theory would not apply to substances more associated in the liquid than in the gaseous condition. In the tables above, 1 to 21, in the columns headed "Crompton" we give the results obtained from this equation for the substances under examination. For additional evidence bearing upon the theory, see Jour. Phys. Chem. April, 1902, p. 219, and Proc. Chem. Soc. Vol. 17, 233, 1901.

It appears that *at low temperatures, where the vapor pressure is small, the results are invariably, and usually very considerably, too large. But at the highest temperature examined for each substance the agreement is good*, the divergence at this temperature being greater than one calorie only in the cases of ether, normal octane, stannic chloride, and four of the five associated substances.

The results therefore merit detailed study. Of the twenty-one substances, twelve, viz: ether, di-isopropyl, isopentane, normal pentane, normal hexane, benzene, hexamethylene, fluobenzene, chlor-benzene, brom-benzene, iodo-benzene, and carbon tetrachloride, give results that are in all respects similar. With them at the low temperatures Crompton's theory gives too high results, but as the temperature is raised the results grow in the main continually closer to those given by the thermodynamical equation. For these substances after a vapor pressure of 7000 mms has been reached, it may be said that Crompton's theory gives a very fair approximation, usually within one calorie, to the results obtained thermodynamically.

Di-isobutyl, normal heptane, and normal octane, each show a good agreement at the lowest temperature for which the vapor pressure was measured, viz: 100°, 80°, and 120°. Then with increasing temperature Crompton's equation gives results lower than those obtained thermodynamically.

Stannic chloride is similar to the above in showing better agreement at the lower temperatures than at the higher, but in this case Crompton's results are uniformly the larger.

In the case of water the results of Crompton are always the larger, but had the observations been continued nearer the critical temperature, it is quite possible that good agreement would have been reached.

With the three alcohols, Crompton's equation gives entirely too high results at the lower temperatures. Then with rise in temperature the results from Crompton's equation becomes decidedly the lower, but near the critical temperature the difference is not very marked.

With acetic acid, Crompton's equation gives results more than twice too large at the lowest temperature. As the temperature is raised the disagreement becomes continually less. It must be borne in mind that acetic acid vapor shows marked association.

Comparing the three equations the value of Crompton's theory becomes doubly apparent. Crompton's equation does not involve the vapor pressure, and therefore, if trustworthy, will act as a check upon the thermodynamical equation at the end-points of the curve, where owing to the manner of obtaining the  $\frac{\partial P}{\partial T}$  the thermodynamical results are somewhat uncertain.

On the other hand, compared with equation 4, Crompton's theory does not depend upon the attraction and would not be affected by a variation of the attraction with the temperature. It should therefore furnish a clue to those substances in which the molecular attraction does not remain constant with increasing temperature.

At low temperatures Crompton's equation gives values uniformly too high, and it therefore cannot be used to check the results of the other equations. But at the highest temperatures the evidence obtained from the results is exceedingly interesting. For ether, di-isopropyl, isopentane, normal pentane, normal hexane, benzene, hexamethylene, fluo-benzene, and carbon tetra-

chloride, Crompton's equation gives results in better accord with the values obtained from equation 4 than with the thermodynamical results. For these substances at the highest temperatures considered, Crompton's theory gives results differing in no case from those of equation 4 by so much as 0.4 of a calorie, and in several cases the agreement is almost exact. This is splendid confirmation of our belief that in these cases the divergences in the constant of equation,  $\frac{L - E_1}{\beta^2 d - \beta^2 D} = \text{constant}$ , were due to the Biot formula from which the  $\frac{\partial P}{\partial T}$  was obtained.

For di-isobutyl, normal heptane, and normal octane, Crompton's equation does not confirm the results of equation 4 when the constants that we have adopted are used, but points instead to lower values for these constants, and we would here call attention to the fact that this indication meets further confirmation. (Cf. results equations 20, 21 and 25.)

For chlor-benzene, brom-benzene, and iodo-benzene, Crompton's theory points to higher constants. This evidence cannot be entirely trusted since the highest measurements for these substances are considerably below the critical temperature.

For stannic chloride, Crompton's equation confirms in a measure the constant adopted. This was a surprise, and suggests the possibility of an error in the Biot formula used.

For the alcohols and acetic acid, Crompton's equation confirms the belief that in these substances the molecular attraction changes at high temperatures.

To consider the question as to why Crompton's theory does not give correct results at low temperatures we would call attention to the fact that Mr. Crompton could as well have taken the law of vapor pressure as  $PV = P_1 V_1$  and have obtained,

$$(10) \quad L = 2P_1 V_1 \log. \frac{d}{D}.$$

Here  $V_1$  is the volume of the liquid and  $P_1$  is the theoretical pressure of the liquid. In calculating this theoretical pressure it will be seen that the equation cancels back to its original form,

$2 RT \log_e \frac{d}{D}$ . We have here called attention to the transposition only that the equation might be recognized as identically the same equation with which we have to deal in the Joule-Thomson effect of the free expansion of gases. The Joule-Thomson energy change is in reality a latent heat — the very same effect of the Crompton equation, only the compression is not carried to liquefaction. That effect has been but little studied and is usually laid entirely upon cohesive forces. This may not be the case, and certainly is not the case when hydrogen, which gives negative results, is considered. We here point out that *if it is experimentally possible, a continuation and extension of the experiments of Joule and Lord Kelvin in connection with the theory of Crompton, should enable Crompton's theory to be understood and correctly modified.*

If the PV curves, Diagrams 1 to 3, be examined in connection with Crompton's equation, it will be noted that Crompton's equation usually gives good agreement with the thermodynamical results at points corresponding to the descending portions of those curves.

#### **The Variation of the Heat of Vaporization with the Temperature**

The discussion in this and the previous paper of the data bearing upon the latent heats of vaporization obtained for the twenty-one substances examined cannot have failed to impress one with the wonderful accuracy of the measurements by Profs. Ramsay and Young and by Prof. Young, upon which that data is based. The data upon heats of vaporization here made available is therefore the most extensive and the most accurate yet published. The variation of the latent heat with the temperature has always been a question of interest, and we therefore attempt to show most clearly the manner of this variation.

The function of a portion of the latent heat is well known. It is expended in overcoming the external pressure. The portion so expended can be calculated and neither theoretically nor actually does it appear to be a simple function of the temperature. We have called the energy so expended  $E_p$  and have

given its value for each substance and temperature examined. (See Second paper, Tables 2 to 22, under heading  $E_v$ .)

It has been suggested that  $\frac{E_v}{L}$  is a constant. Since  $E_v$  is  $0.031833 P(V-v)$  and  $L = 0.031833 T \frac{\partial P}{\partial T}(V-v)$ , this would require that  $\frac{E_v}{L} = PT \frac{\partial P}{\partial T} = \text{constant}$ . This relation is not confirmed. Examination shows that  $E_v$  first increases and then decreases with the temperature, while the latent heat, almost invariably, decreases.  $E_v$  thus varies independently of the latent heat and ranges usually between seven and fourteen percent of its value.

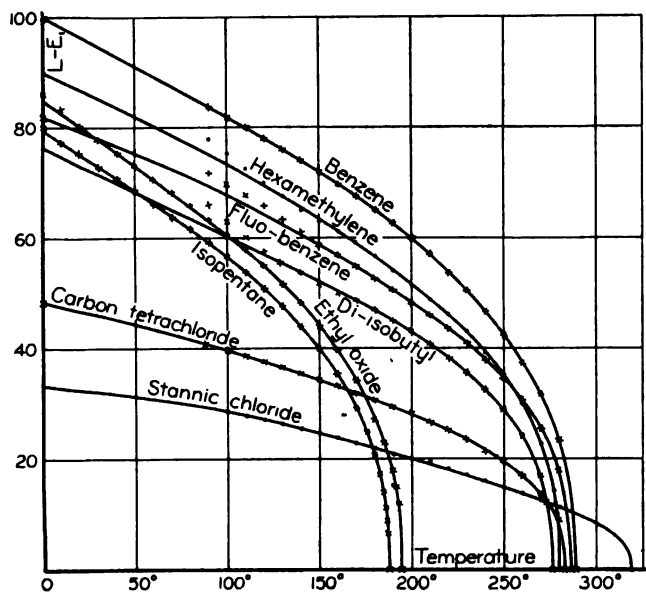


Diagram 8

Ordinates give internal heat of vaporization in calories

It was therefore thought best to subtract from the total latent heat this variable amount of energy thus externally expended and to plot the internal latent heat of vaporization against the temperature. The values are given in Second



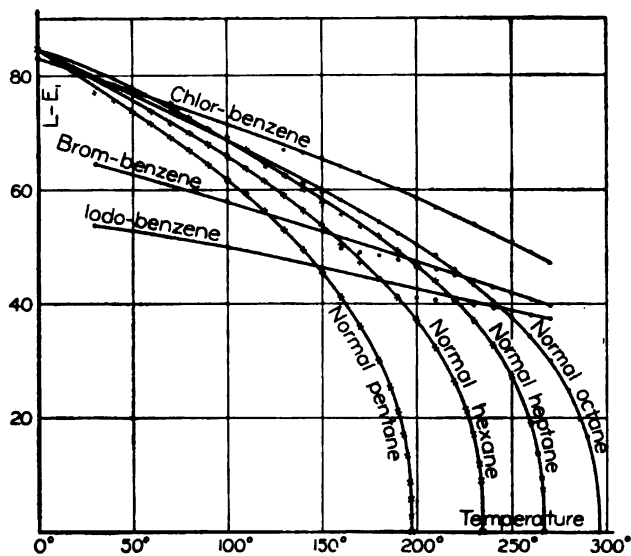


Diagram 9

Ordinates give internal heat of vaporization in calories

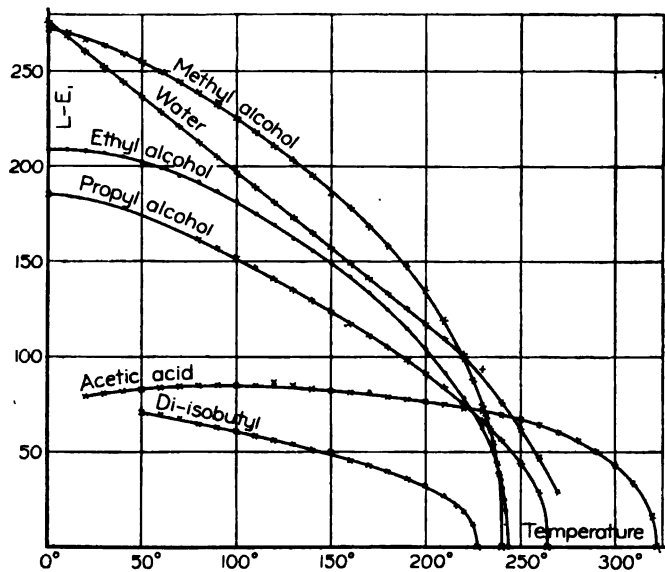


Diagram 10

Ordinates give internal heat of vaporization in calories

paper, Tables 2 to 22, under the heading  $L - E_r$ . The curves are shown in Diagrams 8, 9, and 10. The observations are marked with dots, circles or crosses. The scale needs no explanation except that for water 300 should be added to the ordinates to make the reading as expressed in calories correct.

It will be noted :—

1. That the internal latent heat cannot be regarded as a linear function of the temperature except at low vapor pressures and for a limited range of temperature. Water does show a linear variation to  $230^\circ$ , but this is due to Regnault's linear formula from which the values were obtained. The values obtained from Ramsay and Young's observations above  $230^\circ$  show beyond question that the line for water should also curve perceptibly before that temperature is reached.

2. The curves are all concave towards the temperature axis. Hexamethylene, di-isobutyl, brom-benzene, and iodo-benzene would not always be concave if the observations were exactly followed. But the diagrams themselves add strongly to evidence already pointed out (p. 595, etc.) in indicating that these values need further study.

3. Except in the case of acetic acid, the internal latent heat always decreases with the temperature.

4. Several attempts to find a simple empirical formula connecting the internal latent heat and the temperature failed. The investigation was not pushed.

#### Some Relations Resulting from the Latent Heat Equations

By combining equations 6 and 7, we get :—

$$(11) \quad P = \frac{\partial P}{\partial T} T - \frac{\mu' (T^3 d - T^2 D)}{0.031833(V - v)}, \text{ or,}$$

$$(12) \quad P = \frac{\partial P}{\partial T} T - \frac{31414 \mu'}{Vv^3 + V^{\frac{1}{2}}v^3 + V^{\frac{1}{2}}v}.$$

Equations 11 and 12 are not suitable for calculating accurately the pressure, for that value appears as the difference of two comparatively equal values. We give as an example of such application Table 22 below. Of the substances we have dis-

cussed isopentane is one of the most carefully measured and the agreement is to within the limit of experimental error permitted by the equation. The  $\frac{\partial P}{\partial T}$  is obtained from Biot's formula.

$\frac{31414 \mu'}{V_v^{1/2} + V_v^{1/2} + V_v^{1/2}}$  is given under the heading "a."

TABLE 22

## Isopentane

Temperature	$\frac{\partial P}{\partial T}$	$\frac{\partial P}{\partial T}$	a	Pressure	
				Calculated	Biot
0	11.16	3047	2742	305	258
20	21.04	6165	5639	526	573
40	35.66	11162	10139	1023	1131
60	55.73	18558	16634	1924	2036
80	81.85	28893	25541	3352	3401
100	114.70	42783	37310	5473	5354
120	155.18	60986	52480	8506	8040
140	204.42	84425	71920	12505	11620
160	264.0	114312	96810	17502	16285
180	335.9	152163	132410	19753	22262
187.8	367.8	169480	159420	10060	25005

Equation 12 will recall the similar equation:—

$$(13) \quad p = bT - a,$$

proposed by Profs. Ramsay and Young,<sup>1</sup> where  $b = \frac{\partial P}{\partial T}$  and  $a =$  constant. The equation is applicable where the volume of the gas is kept constant. "a" has a value dependent upon the volume.

The  $\frac{\partial P}{\partial T}$  of equation 12 shows the variation of the vapor pressure of a liquid with a rise in temperature, the volume of the liquid meanwhile undergoing change. The  $\frac{\partial P}{\partial T}$  of equation 13 de-

<sup>1</sup> Phil. Mag. May, 1887. Phil. Mag. August, 1887. Proc. Phys. Soc. 1894-95. Proc. Phys. Soc. Vol. 15. Phil. Mag. April, 1899. Proc. Phys. Soc. Vol. 17.

notes a change in pressure of a gas, the volume being kept constant. A liquid cannot exist above its critical temperature and at that point the liquid and its vapor are identical. The critical temperature therefore marks the limit for which the  $\frac{\partial P}{\partial T}$  of equation 12 can be obtained, but just at that point the  $\frac{\partial P}{\partial T}$  of the liquid and the  $\frac{\partial P}{\partial T}$  of its vapor at constant volume must be identical.

That the  $\frac{\partial P}{\partial T}$  obtained from the Biot formula could not in the nature of the case be accurate at or near the critical temperature we have already pointed out. (Second paper, p. 395.) That the variation we were there led to expect is quantitatively equal to the actual variation as found for equation 13, we have subsequently shown (p. 594). It remains to be seen if "*a*" of equation 13 corresponds to the function  $\frac{31414 \mu'}{Vv^{\frac{1}{2}} + V^{\frac{1}{2}}v^{\frac{1}{2}} + V^{\frac{1}{2}}v}$  of equation 12.

At the critical temperature  $v = V$ , and therefore we have at that point,

$$(14) \quad a = \frac{10471 \mu'}{V^{\frac{1}{2}}}.$$

Choosing isopentane as being one of the most carefully measured substances, we found for  $\mu'$  the value 105.4 (Table 25) and  $V$  is 4.266. "*a*" therefore becomes 159,400. The values given by Dr. Young<sup>1</sup> at volume 4.3 are 157,880 from drawn isochors, and 162,890 when calculated from some values of  $b$ . The agreement in this instance is therefore to be regarded as perfect.

That the laws of attraction we have assumed enable the constants of the equation of Ramsay and Young at one point to be foreseen and calculated is proof of the most convincing nature that the theory of the attraction outlined is correct. We are led to believe that, properly modified, the same considerations

<sup>1</sup> Proc. Phys. Soc. 1894-95, p. 654.

will elsewhere be successful in a further calculation of these constants. The relation is so full of possibilities and for its adequate consideration will require so extended an investigation that we postpone the discussion for a separate paper.

Again, combining equations 6 and 8 we obtain: —

$$(15) \quad \frac{\partial P}{\partial T} = \frac{287500}{m} \log \frac{V}{V - v}$$

Owing to the inaccuracy of Crompton's equation at low vapor pressures at such points equation 15 cannot give accurate results. But as the critical temperature is approached we believe that this equation offers the most accurate method yet available for finding the  $\frac{\partial P}{\partial T}$ , giving results far better than could be obtained from direct observations of the pressure even when the observations are afterwards smoothed.

In Table 23 below we apply the equation to isopentane, comparing the results obtained by its aid with those obtained from Biot's formula.

TABLE 23

## Isopentane

Temperature	$\log \frac{V}{v}$	$V - v$	$\log \frac{V}{V - v}$	$\frac{\partial P}{\partial T}$ from Equation 15	$\frac{\partial P}{\partial T}$ from Biot
0	2.768	915.8	0.003022	12.05	11.16
20	2.419	422.4	0.005725	22.83	21.04
40	2.126	221.5	0.009598	38.27	35.66
60	1.868	126.2	0.01480	59.00	55.73
80	1.635	76.1	0.02147	85.61	81.85
100	1.417	47.56	0.02980	118.82	114.70
120	1.206	30.20	0.03993	159.22	155.18
140	0.9920	19.00	0.05221	208.16	204.42
160	0.7612	11.34	0.06712	267.6	264.0
180	0.4442	5.09	0.08728	348.0	335.9
187.4	0.1508	1.503	0.1003	399.9	366.4
187.8	—	—	0.1018	405.9	367.8

At the critical temperature the fraction  $\frac{\log \frac{V}{v}}{V-v}$  assumes the indeterminate form  $\frac{0}{0}$ . Evaluating by differentiating the numerator and denominator we find the limit approached at the critical temperature to be  $\frac{0.4343}{V}$ , 0.4343 being the modulus of the Napierian system of logarithms. Therefore we have at the critical temperature,

$$(16) \quad \frac{\partial P}{\partial T} = \frac{124860}{mV},$$

a very simple relation. For isopentane we thus get the values of  $\frac{\partial P}{\partial T}$  as 405.9, a result in exact accord with the values 397 to 407 as given by Dr. Young,<sup>1</sup> and thus confirming every conclusion we have hitherto drawn relative to the value of  $\frac{\partial P}{\partial T}$  at this point.

Combining equation 16 with 12 and remembering that at the critical temperature  $V = v$  we have,

$$(17) \quad P = \frac{124860T}{mV} - \frac{10471\mu'}{V^{1/2}}.$$

Applying this equation to isopentane, we have,  $V = 4.266$ ,  $m = 72.1$ ,  $T = 460.8$ ,  $\mu' = 105.4$ , and the pressure thus calculated is 27600 against 25000 observed, an agreement well within the limit of experimental error, since the pressure is found as a difference.

A more general equation is obtained by combining equations 7 and 8 to obtain

$$(18) \quad P = \frac{31414}{V-v} \left\{ \frac{9.1522}{m} T \log \frac{V}{v} - \mu' (p'd - p'D) \right\},$$

an equation, which owing to the divergence shown by Crompton's theory is not applicable to low pressures.

We have purposely omitted all reference to those equations

<sup>1</sup> Proc. Phys. Soc. 1894-95, p. 650.

connecting the latent heat with the specific heat of liquid or vapor, as it is our purpose at a future time to point out a relation existing between the specific heat of solid, liquid, and vapor, and to discuss such equations in that connection.

#### A Further Application of Crompton's Theory to Verify the Proposed Law of Molecular Attraction

Following a line of argument already advanced,<sup>1</sup> if we consider any gas it is reduced to the liquid state by pressure and by the molecular attraction. In nature the two, pressure and attraction, act jointly and continuously. But theoretically we can separate their action, since mechanically all forces are independent of each other. Legitimately then, we can consider a liquid at its critical temperature as reduced to that density: First, by the action of a pressure; second, by the action of molecular attraction. Accordingly the theoretical density of the gas at its critical temperature and under its critical pressure was calculated. *The gas would be reduced to that condition if there were no molecular attraction. The remainder of the condensation, to the actual density, must be the work of the attraction alone.*

The theoretical critical density can be calculated by the equation,

$$(19) \quad D = 0.016014 \frac{Pm}{T}.$$

If the attraction obeys the law assumed we can use equation 2 to calculate the energy necessary to overcome the attraction and expand the gas from its observed to its theoretical density. If to the energy so calculated we add the energy necessary to overcome the external pressure during the change in volume, we have the total energy,  $\lambda + E_1$ , required by the change. The equation will become,

$$(20) \quad \lambda + E_1 = \mu' (v^3 d - v^3 D) + 0.031833 P \left( \frac{1}{D} - \frac{1}{d} \right) \text{ Cals.}$$

By Crompton's theory we can calculate the energy neces-

<sup>1</sup> Jour. Phys. Chem. 6, 223 (1902).

sary to change the gas from its observed to its theoretical density as if the change were produced by pressure alone, the equation being :—

$$(21) \quad L = \lambda + E_1 = \frac{9.1522}{m} T \log \frac{d}{D} \text{ Cals.}$$

In these equations  $T$  is the critical temperature,  $d$  denotes the critical density, and  $D$  is the theoretical density of the vapor at the critical point.

The results of equation 20 are given below in Table 24 under heading Mills. The results from equation 21 are given under the heading Crompton. The difference is also given. The agreement is as perfect as could be desired. The difference is usually less than one calorie and amounts to a divergence of more than four percent only in the case of normal octane and the associated substances. (To these latter neither theory is applicable.)

With the three alcohols others have concluded that at the critical temperature *there is no association*. With them the molecular attraction, it will be recalled, changed with the temperature. Using the values of  $\mu'$ , obtained nearest the critical temperature, where the effect of the association could be assumed *nil*, we obtained the last values given, which are in good accord with the results given by Crompton.

In Table 24 the critical data, except for water, are from the measurements of Profs. Ramsay and Young or Dr. Young. References have been given. (Second paper.)

There is nothing in the method adopted to prevent the application of equations 20 and 21 to other points than the critical temperature. Had the equations been combined, an equation similar to equation 18 would have been produced, and the above results may be regarded as but a special application of that equation.



TABLE 24

Substance	Molecular weight	$\mu'$	Critical			Theoretical density
			Temperature	Pressure	Density	
Ether	74.08	104.4	194.0	27060	0.2463	0.06873
Di-isopropyl	86.11	98.08	227.35	23330	0.2411	0.06430
Di-isobutyl	114.14	86.30	276.8	18640	0.2366	0.06197
Isopentane	72.10	105.4	187.8	25005	0.2344	0.06266
Normal pentane	72.10	109.9	197.2	25063	0.2324	0.06157
Normal hexane	86.11	102.85	234.8	22433	0.2343	0.06093
Normal heptane	100.13	98.75	266.9	20399	0.2344	0.06057
Normal octane	114.14	93.00	296.2	18734	0.2327	0.06015
Benzene	78.05	109.5	288.5	36395	0.3550	0.08100
Hexamethylene	84.10	103.6	279.95	30234	0.2733	0.07365
Fluo-benzene	96.09	85.60	286.55	33912	0.4107	0.09325
Chlor-benzene	112.5	81.19	360.7	33962	0.4179	0.09554
Brom-benzene	157.0	56.12	397.0	33912	0.5695	0.12730
Iodo-benzene	203.9	44.40	448.0	33912	0.6826	0.1536
Carbon tetrachloride	153.8	44.09	283.15	34180	0.6536	0.1514
Stannic chloride	260.8	26.04	318.7	28080	0.8621	0.1982
Water	18.02	553.3	364.3	148200	0.429	0.06707
Methyl alcohol	33.03	305.0	240.0	59759	0.2715	0.05974
Ethyl alcohol	46.05	241.2	243.6	47700	0.2857	0.06809
Propyl alcohol	60.06	199.2	263.7	38120	0.2778	0.06830
Acetic acid	60.03	130.0	321.65	43480	0.3506	0.07025
Methyl alcohol	—	259.4	—	—	—	—
Ethyl alcohol	—	197.2	—	—	—	—
Propyl alcohol	—	157.0	—	—	—	—

TABLE 24—(Continued)

Substance	$F_v$	$\rho^3 d - \rho^3 D$	$\lambda$	Latent heat		$\Delta$
				Mills	Crompton	
Ether	9.03	0.2173	22.69	31.72	31.98	-0.26
Di-isopropyl	8.46	0.2218	21.75	30.21	30.52	-0.31
Di-isobutyl	7.07	0.2228	19.23	26.30	25.65	0.65
Isopentane	9.30	0.2194	23.11	32.41	33.51	-1.10
Normal pentane	9.52	0.2199	24.17	33.69	34.42	-0.73
Normal hexane	8.67	0.2230	22.93	31.60	31.57	0.03
Normal heptane	7.95	0.2239	22.11	30.06	29.00	1.06
Normal octane	7.35	0.2233	20.77	28.12	26.82	1.30
Benzene	11.04	0.2754	30.14	41.18	42.26	-1.08
Hexamethylene	9.55	0.2298	23.80	33.35	34.27	-0.92
Fluo-benzene	8.95	0.2898	24.81	33.76	34.30	-0.54
Chlor-benzene	8.62	0.2889	23.45	32.07	32.81	-0.74
Brom-benzene	6.59	0.3258	18.28	24.87	25.41	-0.54
Iodo-benzene	5.45	0.3450	15.32	20.77	20.97	-0.20
Carbon tetrachloride	5.52	0.3348	14.76	20.28	21.02	-0.74
Stannic chloride	3.47	0.3686	9.60	13.07	13.25	-0.18
Water	59.29	0.3479	192.5	251.8	260.9	-9.1
Methyl alcohol	24.84	0.2566	78.26	103.10	96.35	6.75
Ethyl alcohol	16.99	0.2502	60.35	77.34	63.94	13.50
Propyl alcohol	13.39	0.2437	48.55	61.94	49.81	12.13
Acetic acid	15.75	0.2925	38.02	53.77	63.27	-9.50
Methyl alcohol	—	—	66.55	91.39	—	-4.96
Ethyl alcohol	—	—	49.34	66.33	—	2.39
Propyl alcohol	—	—	38.25	51.64	—	1.83

### Extension of the Theory to the Energy Relations at the Critical Temperature

Solving equation 6 of the first paper<sup>1</sup> we get :

$$(22) \quad \mu = c \cdot \frac{L - E_1}{r_d - r_D} r^2 m = c \mu' r^2 m,$$

where  $c$  is the same constant for all non-associated substances, and  $m$  is the molecular weight.  $\frac{L - E_1}{r_d - r_D}$  we have shown to be a constant for any particular substance, have called this constant  $\mu'$ , and have given the average constants for the substances examined. (Table 25.)  $\mu$  represents the absolute attraction at unit distance from a molecule and must be regarded as an exceedingly important and a constant property of the molecule. The values obtained for  $\frac{\mu}{c}$  are given in Table 25.

We would here call attention to the fact that for bodies of similar constitution and closely related chemically the values of  $\mu$  may be the same, though the observations are not sufficiently extended to permit of any definite conclusion. Thus :—

Normal pentane,	-	-	-	457.3
Normal hexane,	-	-	-	454.2
Normal heptane,	-	-	-	458.6
Normal octane,	-	-	-	451.1
But isopentane,	-	-	-	438.6

It is well also to note that for the associated substances, water, the alcohols, and to a less degree for acetic acid where it is less associated, the values for  $\mu$  are greatly larger than for the other substances examined, and this very large attraction is suggestive in view of the conclusion drawn in the Second paper that quite possibly the molecular association of these substances was caused by the molecular attraction.

Resuming a line of argument followed in the first paper (p. 228) we can test our conclusions further. In a gas indefinite expansion takes place as the pressure is decreased. This shows

<sup>1</sup> Jour. Phys. Chem. 4, 209 (1902).

that the attraction between the molecules cannot be great enough to make the paths of the molecules closed curves. In a liquid, while undoubtedly many molecules whose velocity is above the average molecular velocity, are continually flying away from the surface, yet it must certainly be the case that most of the molecules are drawn back by the molecular attraction. There must be for each substance a certain temperature at which the molecular attraction, without outside pressure, is just strong enough to overbalance the kinetic translational energy of the average particle and cause it to return to the liquid or solid substance. At this point, if the attraction varies inversely as the square of the distance between the molecules, we will have from mechanics,

$$(23) \quad V'^2 = 2 \frac{\mu}{R},$$

where  $V'$  is the molecular velocity and  $R$  is the distance apart of the molecules.  $\mu$  is the absolute attraction at unit distance.

It is a common text book idea that at the critical temperature the kinetic energy of the molecules of a liquid (gas) under the critical temperature just balances the attraction. The idea rests on the diminution and final disappearance of surface tension at the critical temperature, and the fact, that a liquid at its critical temperature may be changed to a gas without the addition of external energy, i. e., by an infinitesimal change in pressure, the heat of vaporization being zero. It must then be at this point that equation 23 will hold good. Putting therefore for the molecular velocity,  $V'$ , its value at this point,  $\sqrt{\frac{3R_c T}{m}}$  (derived as usual,  $R_c$  being 83,250,000) and for  $R$  its value  $c\sqrt{\frac{m}{d}}$ , the constant  $c$  being unknown, but equal for all substances, we get finally,

$$(24) \quad \mu = c' \frac{T}{m} \sqrt[3]{\frac{m}{d}}.$$

In this equation  $T$  and  $d$  denote respectively the critical temperature and density, and  $c'$  is the same for all substances.

Using the values for the critical constants as given in Table 24, we obtain for  $\frac{\mu}{c}$  the values given in Table 25.

Now if our ideas are correct and the absolute attraction  $\mu$ , given in equations 22 and 24 are the same, and correctly measured, we have a right to combine these equations and get : —

$$\frac{\frac{\mu}{c}}{\frac{\mu}{c'}} = \text{constant} = \frac{\frac{L - E_1}{T} \sqrt{\frac{m}{d}}}{\frac{L - E_1}{T} \sqrt{\frac{m}{d}}}, \text{ or,}$$

$$(25) \quad \frac{m\mu' \sqrt{d}}{T} = \text{constant},$$

where  $T$  must be the critical temperature and  $d$  must be the critical density.

If therefore the values of  $\frac{\mu}{c}$  given in Table 25 be divided by the values of  $\frac{\mu}{c'}$  given in the same table, the results should prove constant for all non-associated substances. The result of this division is given in Table 25.

The mean value for the non-associated substances is 10.76. Since the values for  $\mu'$  are uncertain by about two percent, and since the critical data cannot be measured accurately, the close agreement can be regarded as exceedingly satisfactory. A review of the data leads the author to believe that isopentane and normal octane are the only variations that are not due largely to the values adopted for  $\mu'$ .

Associated substances, *a priori*, could not agree with the equation deduced and they do not. But considering them more particularly it will be seen that if at the critical temperature the molecular association had vanished (as is said to be the case for the alcohols), equation 24 would hold. If instead of the average value obtained for  $\mu'$  at the lower temperatures, we use the values for the constant obtained near the critical temperature, equation 22 should also hold, simultaneously with equation 24. For water the data near the critical temperature is lacking, but

making use of the proper values for the alcohols, we obtain the results given in Table 25. These results would evidently be somewhat better if the observations of  $\mu'$  could have been obtained yet nearer the critical point, and we are thus led to regard these associated substances as giving a very remarkable confirmation of the theory.

TABLE 25

Substance	$\mu'$	$\mu$ c	$\mu$ c'	Ratio of $\mu$ to $\mu'$
Ether	104.4	438.5	42.23	10.38
Di-isopropyl	98.08	433.1	41.23	10.51
Di-isobutyl	86.30	418.6	37.78	11.08
Isopentane	105.4	438.6	43.14	10.17
Normal pentane	109.9	457.3	44.15	10.36
Normal hexane	102.85	454.2	42.24	10.75
Normal heptane	98.75	458.6	40.62	11.29
Normal octane	93.00	451.1	39.34	11.47
Benzene	109.5	468.0	43.415	10.78
Hexamethylene	103.6	453.8	44.38	10.23
Fluo-benzene	85.60	392.3	35.86	10.94
Chlor-benzene	81.19	391.9	36.38	10.77
Brom-benzene	56.12	302.8	27.76	10.91
Iodo-benzene	44.40	261.3	23.64	11.05
Carbon tetrachloride	44.09	236.2	22.32	10.58
Stannic chloride	26.04	166.4	15.23	10.93
Water	553.3	1450.8	123.00	11.79
Methyl alcohol	305.0	968.6	78.56	12.34
Ethyl alcohol	241.2	864.5	61.04	14.16
Propyl alcohol	199.2	780.1	53.64	14.54
Acetic acid	130.0	509.1	55.00	9.26
Methyl alcohol	259.4	823.8	—	10.49
Ethyl alcohol	197.2	706.8	—	11.58
Propyl alcohol	157.0	614.8	—	11.46

It should be noted that the constant obtained from equation 25 and given in Table 25 is just one-half of the constant obtained in Trouton's formula,  $\frac{mL}{T} = \text{constant}$ , where T is the boiling-point of a substance. That there is a reason for this fact we propose later to show in connection with a paper applying the law of attraction to the boiling-point.

In conclusion we again point out that we are indebted to Drs. Ramsay and Young and to Dr. Young, for nearly every measurement used in this article. And we would again express our great appreciation of the accuracy of these measurements and acknowledge our obligation to them.

### Summary

1. Several facts bearing upon the results of the last paper are discussed. These facts confirm the law of attraction assumed by making it most clear that  $\frac{L - E_1}{\frac{1}{d} - \frac{1}{D}}$  does equal a constant (designated  $\mu'$ ), for normally constituted substances, and that the equation is applicable with equal exactness in the immediate neighborhood of the critical temperature.

2. An equation,  $L = 2RT \log_e \frac{d}{D}$ , proposed by Mr. H. Crompton, was investigated, and it was found that at low temperatures, where the vapor pressure is small, the results given by the equation are invariably, and usually very considerably, too large. But at higher temperatures the results are correct.

3. Crompton's equation was shown at the critical temperature to give results confirming the law of attraction assumed. (Equations 20 and 21.)

4. It was shown that,  $\frac{\partial P}{\partial T} = \frac{287500}{m} \log \frac{V}{V - v}$ , within certain limits.

5. It was shown that at the critical temperature the following relations hold true: —

$$(a) \quad P = \frac{\partial P}{\partial T} T - \frac{10471 \mu'}{V^{1/3}},$$

$$(b) \quad \frac{\partial P}{\partial T} = \frac{124860}{mV},$$

$$(c) \quad \frac{m\mu' \frac{1}{d}}{T} = \text{constant},$$

the last being an interesting confirmation of the law of attraction assumed.

6. It was shown that at the critical volume " $a$ " of the equation,  $p = bT - a$ , becomes identical with the term,  $\frac{10471 \mu'}{V^{1/2}}$ .

7. The variation of the latent heat of vaporization with the temperature is discussed.

*University of North Carolina,  
August, 1904.*

### Addendum

Since this paper was written, a letter has been received from Dr. Young, giving the values of the  $\frac{\partial P}{\partial T}$  for ethyl oxide. The pressures given in the original paper are correct as are the values of the  $\frac{\partial P}{\partial T}$  below 180° C. The corrected values above that temperature are given below, together with the corrected values of the heat of vaporization and of  $\mu'$ .

Temperature	$\frac{\partial P}{\partial T}$ corrected	L	$L - E_1$	$\mu'$
185°	354.9	26.18	22.36	97.7
190	374.1	19.21	16.42	96.4
192	382.2	14.66	12.52	93.5
193	385.8	11.17	9.53	90.7
194	389.8	—	—	—
194.45	391.6	—	—	—

Dr. Young gives 194.45° as probably very nearly the true critical temperature, and 3.814 as the true critical volume of a gram. By interpolation of the results given by Profs. Ramsay and Young (Phil. Mag. May, 1887, p. 441) for the equation  $P = bT - a$ , the true value for the  $\frac{\partial P}{\partial T}$  at this volume appears to

be 436. Thus the  $\frac{\partial P}{\partial T}$  from Biot's formula at the critical temperature is about ten percent too low, an amount which is not quite sufficient to explain the decrease in the value of  $\mu'$  at the higher temperatures. But above 180° C, owing to the hydrolysis



of the methyl salicylate used as a heating jacket, the data is somewhat uncertain.

It should be noticed that equation 14 of the present paper gives 441.9 as the value of the  $\frac{\partial P}{\partial T}$  at the critical temperature, a result which agrees well with the value 436 given below, thus confirming what has been said as to the accuracy of that equation.

*November 1, 1904.*

## PHYSICAL CHEMISTRY IN THE SERVICE OF AGRICULTURE<sup>1</sup>

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BY F. K. CAMERON

There is some difficulty in approaching this subject, for the reason that what constitutes agricultural chemistry can not be clearly defined, and the boundary lines between it and other branches of applied chemistry are not always evident. Much of biological chemistry and much of geological chemistry, lines along which notable achievements have been made by the applications of the principles and methods which in recent years have come to be called physical chemistry, could with propriety be claimed also for agricultural chemistry. One finds agricultural chemists engaged in the examination of drugs, fertilizers, leathers, and tannins, etc., as well as in the examination of foods or soils. Important applications of physical chemistry are to be found along many of these lines, which might be claimed for the agricultural chemist, but disputed as belonging to the field of the industrial chemist, or others. The manufacture of nitric acid by electrochemical methods, while a problem of industrial chemistry, is important because of the use of nitrates in agriculture. But confining oneself strictly to the work professedly done in the immediate interests of agriculture or farm practices, there is to be found much evidence of the increasing influence of physical chemistry.

In common with other branches of applied chemistry, agricultural chemistry has acquired much for its analytical processes from the work of the physical chemists. Applications of the solubility laws, of the principles of mass action or reaction velocities to precipitation processes, color changes, etc., are the common property of analytical chemistry in which the agricultural chemist shares. Viscosity, specific gravity, optical rota-

<sup>1</sup> A paper read before the Physical Chemistry Section of the International Congress of Arts and Sciences at St. Louis.

tion, indices of refraction, freezing-points and boiling-points of mixtures and solutions, the distribution of a solute between non-consolute solvents, are all used more or less commonly by agricultural chemists in operations with which they specially have to deal, and the mechanisms of the processes actually employed are very largely determined by the researches of those who have developed the science of physical chemistry.

But aside from strictly analytical features, physical chemistry has suggested and aided developments in agricultural research. Without attempting to give an exhaustive résumé of the entire field, brief attention may be called profitably to a few examples in which physical-chemical principles are, or may be, aids to the study of agricultural problems.

The determination of the heats of combustion in connection with the food work of both man and other animals is a physical-chemical problem and an agricultural one now receiving a great deal of attention. It is believed to be of far-reaching importance in the development of our civilization. The very important work of Atwater with human beings, and the similar work of Armsby with farm animals in the respiration calorimeter is very largely governed by physical-chemical considerations.

The effect of pressure upon chemical processes, either between mineral components or upon processes induced by organisms, is now receiving attention, as witness the work of Hite upon the changes occurring in milk.

One of the most important problems in agricultural chemistry is that of the adsorptive effect of the surfaces of soil particles upon other substances. It is well known that finely divided particles have the power of concentrating in the atmosphere around them moisture vapor, carbon dioxide, and other gases and that the amount of this effect varies not only with the extent of surface exposed by the particles, or their degrees of fineness, but also with the nature of those surfaces as well as the nature of the gases themselves. This action is a selective one, some gases being removed from a mixture more readily than

others. The adsorption or concentration produced by solid quartz in the case of carbon dioxide is quite small, while with powdered charcoal it is large, and with soils it varies within rather wide limits—a matter of considerable importance to some plants which are seemingly much affected by the composition of the soil atmosphere. In a manner apparently analogous to the adsorption of such constituents from the atmosphere, finely divided particles, such as are found in soils, show an apparent selective adsorption for dissolved substances, the most familiar example being the adsorption of coloring materials from solution by charcoal. It was early shown by Liebig, Way, and others, that soils show this action upon dissolved mineral salts, frequently in a very marked way, and not only do they possess the power of abstracting individual salts from a solution of several salts, but they seem to possess the power of selecting constituents from the component salts of the mixtures. This is strikingly shown in the case of ammonium salts when passed through a soil, ammonia being very largely retained, while the acid residue accumulates in the leachings. Potassium and phosphoric acid seem in general to be adsorbed far more readily and to a greater extent than other common mineral constituents. That great differences exist in the adsorptive power of different soils and also in their action upon different salts and the constituents of these salts is well known, and this is obviously of very great importance for the practice of fertilizing with mineral salts. The study of the phenomena is a rather complicated one, largely owing to the metathetical reactions and mutual replacements between the soil components and the other solutes, but it offers interesting mass action and electrolytic dissociation problems which should appeal to the physical chemist. The selection of one constituent of a salt in preference to another seems to be dependent upon the amount of dissociation of the dissolved salts, an interesting subject which has not as yet been worked out. Salts which are hydrolyzed readily show this separation of constituents by adsorption most markedly. Flocculation and deflocculation of clays and colloids and similar material,

which is now receiving much attention by physical chemists, is of the first importance to agriculture, and in fact much of the progress which has been made in this line of investigation has resulted from work done primarily for agriculture, as in the case of the magnificent researches of van Bemmelen.

It is now generally recognized that the immediate source of the food of plants (excepting of course the carbon dioxide absorbed from the atmosphere by leaves) is the soil moisture or soil solution and that before any mineral or other plant food can be absorbed or taken up by the plant it must be first dissolved. It has been aptly said that the soil is the "stomach" of the plant where its food is prepared and put in solution ready for absorption. From this point of view the problems of plant nutrition, and, to a large extent, fertilizer practices, become solution studies, and, therefore, physical-chemical ones.

It has long been known that the addition of one fertilizer to the soil will frequently cause an increased absorption of other fertilizer constituents by the crop. It has been frequently found, for instance, that the addition of a potash salt to a soil will cause an increased absorption of phosphorus. One of two explanations is generally offered; first, that the potassium stimulates and strengthens the plant so that it can take up and use more phosphorus and can, by the development of a more vigorous root growth, "go after" and obtain the phosphorus which it requires; second, that the addition of the potassium salt increases the solubility of the slightly soluble phosphates in the soil and thus makes them more available, on the principle that the addition of a salt which does not yield a common ion will increase the solubility. Both explanations may be right, so far as they go (although it is interesting to note here that potassium chloride, for instance, appears to decrease the solubility of the phosphates of iron, aluminum or calcium), but neither one nor both is entirely satisfactory in view of such observations as those of Wolff, made as early as 1865, that the absorption by a plant of one salt from a solution may be very materially affected by the presence of another salt, though both be entirely dissolved at the begin-

ning of the experiment. We must for the present admit that there are factors here with which we are poorly equipped to deal. We do not understand why or how the plant can exercise a selective power in absorbing solutes from the nutrient solution in the soil or artificial water cultures, yet there may be very important quantitative relations involved here which should be studied by, or in association with, a physical chemist.

This selective power is one of the difficulties encountered in trying to explain absorption as an osmotic phenomenon, assuming the integument of the root to be a semipermeable membrane. It is conceivable that the plant could thus obtain its needed water from the soil, but not cause the transmission of the solutes, unless our usual conceptions as to the nature and functions of semipermeable membranes are to be materially altered. The conception that we have to deal here with an "imperfect" semipermeable membrane, something which shows a tendency to act as a semipermeable membrane, but leaks, explains anything or everything, and therefore nothing. That the membrane may have two distinct functions, acting as a semipermeable membrane, but also simultaneously exercising some physiological activity toward the solute or that it is only semipermeable to one class of substances (such as organic compounds) and permeable to others (such as mineral salts), may be a better hypothesis, but brings in a concept with which the physical chemist is not prepared to deal at present. The concentration of the root sap is much higher than that of the soil solution, and it is difficult to see how rupture of the root covering could be prevented, should it act as a semipermeable membrane, although a more thorough knowledge of the phenomena of transpiration and guttation, which we know to be frequently large in amount, might offer a satisfactory explanation.

Furthermore, we are troubled as yet by having no clear concept as to what constitutes a plant food, although of course it is but little more than a matter of analysis to determine what elements are involved, and we have some knowledge of their functions, as for instance that of potassium in the development

of starch. But we are as yet utterly in the dark as to whether potassium is taken up as such, perhaps as an ion or in combination as a salt; whether the plant has the power to absorb ions from the solutions, or whether it absorbs salts alone and then excretes a part of them as acids or bases. We know that the plants can absorb organic solutes and use them in metabolic processes, but whether they ever do normally in order to avail themselves of mineral constituents thus combined, or for other reasons, is uncertain. These questions are fundamental ones for plant physiology and for a rational scheme of specialized fertilizer practice, and it does not seem too much to hope that physical chemistry may here furnish suggestions and methods which will enable the physiologist to advance materially a subject of enormous practical as well as theoretical importance.

The soil may be considered as a complex system containing components in three phases, the solid, gaseous, and liquid, the liquid phase as forming a nutrient solution for crop production being the one of immediate interest to agriculture, and the solid and gaseous phases having but little importance except as they affect or determine the liquid phase. Perhaps a distinction should be made as to a fourth kind of matter, the living organisms, in which would be included bacteria, molds, ferments, and enzymes. The difficulty of determining what constitutes the variables in any given soil is generally unsurmountable, and the variance of the system is therefore indeterminable so that no practical applications of the phase rule to a soil system has yet been made satisfactorily. Yet this way of looking at the subject has a real value since it gives a clear, orderly perspective of the problem.

When one attempts to simplify the problem by considering only certain components, other difficulties arise. We know as yet but little of the phenomena exhibited towards a solvent by a mixture of three or more electrolytes; but, even when but two are considered, those with which we are most interested in soil investigations seem to be the ones whose dissociation products do not obey the mass law and give unexpected osmotic pres-

sures. We need a vast deal more information in this field than we now possess, and for solutions of moderately high concentrations as well as for very dilute ones. The greater number of the rock-forming minerals which comprise the inorganic components of the soil are properly to be regarded as electrolytes, but electrolytes which show a slow rate of solution and in the process are more or less completely hydrolyzed. In fact this slow solution and hydrolysis is the main factor in the "weathering" process, the action of carbon dioxide and other solutes being more or less secondary. Here lies a field in which our knowledge is very meager and in which much profitable research could be done. There are almost no data of value concerning the solubility of minerals in water or salt solutions; in the greater part of the work in the past the importance of the time element has not been recognized. We do not even know whether or not the hydrolysis of these substances be a reversible process to which the mass law would be applicable. Certainly the *à priori* indications of the dissociation hypothesis as to the probable effect of other solutes upon the solubility of these hydrolyzing substances are frequently at variance with the observed phenomena, and a most fruitful field for experimental work by the physical chemist is here indicated.

Physical chemistry has opened up another promising field by the work which has been done upon the effect of solutions of electrolytes upon seedling plants, as in the studies of Coupin, Kahlenberg, and True, and others of probably no less importance. Some of this work, as that of Kahlenberg and True, was done primarily as dissociation studies. From this point of view the method has proved unsatisfactory for several reasons. The criteria used as the death point of the plant or the inhibition of the growth of a radical, are hard to determine with exactness. Seedlings of the same plant, of the same age, and apparently the same past history, show idiosyncrasies. The effect of both cation and anion, as well as the undissociated electrolyte, must always be considered, and finally it seems impossible to eliminate entirely consideration of some physiological factor or factors



exhibited by the seedling and probably connected with its selective power in absorbing solutes as food. From the points of view of physiological research or agricultural study, however, this method gives great promise. Using the dissociation hypothesis as a guiding principle, but with the proper reserve as to the validity of its indications until phenomena have actually been observed, its value has already been shown, and much more can be and probably will be done along this line of investigation. Not only has the death limit of plants in solutions of ordinary salts, or mixtures of such salts as are found in the soils of arid regions, been determined, but results of economic importance for the growth or introduction of crops in those areas have been reached and the germination of seeds under these conditions has received attention with reference to the possibility of starting a crop through the temporary alleviation by irrigation of the soil, and dilution of the salts it contains. This work further offers methods which will probably be of great value in controlling the breeding of salt or "alkali" resisting plants. It has generally been observed with these mineral solutes, which prove toxic at some more or less definite concentration, that they are usually stimulating at much higher dilutions, and this fact has promise of having economic importance as to growth and development of field crops; as to the treatment of malt in breweries to save time in the germination period; and in the preparation of seeds before sowing in the field to insure more certain and rapid sprouting. With the employment of some criteria more satisfactory than the death limit it seems probable that very valuable studies could be made on the concentrations which are most conducive to growth, development of fruit, etc., in plants, and economic results obtained for the greenhouse and orchard if not for the field.

Conductivity measurements have proven most useful in soil investigations, as in the method first suggested by Whitney and developed by Briggs, in which the resistance of a soil saturated with water and placed between parallel electrodes was determined. Knowing the amount of water present in the saturated

soil, which can be readily approximated from its texture, the resistance of the soil can be correlated quite closely with the amount of soluble salts present. A compact field apparatus consisting of a hard rubber cell with parallel electrodes, a circular slide wire bridge with dry battery, resistance coils, and other necessary appendages has been devised. This can be taken into the field and a number of samples over a large area can be examined in a day, the results being correlated with and checked by a few laboratory examinations. In this way the alkali maps of the U. S. Department of Agriculture have been prepared. In humid areas where the movement and translocation of soluble salts in the soil is quite small this same bridge arrangement with permanent parallel electrodes gives a ready means of determining and controlling the moisture content in the soil, and this has found important application in greenhouse culture. This same bridge attached to a thermocouple has been successfully used to give approximate temperatures in fermenting, as in tobacco curing. This electrical thermometer is also being used in certain specialized agricultural industries, as in the controlling of the temperature in greenhouse culture and promises to be of value in measuring temperature in silo beds, hay mows, and similar situations where elevated temperatures may develop.

Attention has also been given by several investigators, notably by Elfking Plowman and Stone, to the effect of electrical currents passed through the soil or "ionization of the soil" as it has been termed, in stimulating or otherwise affecting plant growth, suggesting possible applications to greenhouse culture.

Recently Briggs has devised a very accurate and ingenious laboratory method for determining the amount of moisture present in a soil sample by determining its dielectric constant, and in this way the study of the movement of soil moistures, involving some of the most important problems in soil physics and chemistry, promises to be facilitated enormously.

To the cases which have just been cited many others could undoubtedly be added, and it is clear that physical chemistry in the past has had, and in the future must have, an important in-

fluence upon agricultural chemistry. But nevertheless the retrospect leaves much to be desired and is not altogether inspiring.

Physical chemistry has not yet directly produced any new methods or important modifications in agricultural practice. The number of agricultural investigators whose work shows an appreciation of, or consideration for, the principles or methods of physical chemistry is small, perhaps less than in any other field of applied chemistry. Some of the reasons for this are not far to seek.

Agriculture is a very old art. It has the conservatism of old age and long practiced methods. Those engaged in its service, through the field of applied science, are more or less affected by this conservatism, and it must be admitted that the agricultural chemist as a class is in harmony with his environment. Conservatism may often be a good thing and perhaps it never does really stop progress, but it may certainly delay it. Agricultural chemistry can furnish as proud a list of names of masters from Liebig to the present day, as any field of science. But the work of the present generation is almost entirely along conservative lines, already well marked out, and those who are attempting to apply the principles of modern chemistry to the problems which confront them are comparatively few. This condition is well exemplified in the instruction given to our agricultural students. So far as the speaker is aware, Hall's recent book on the "Chemistry of the Soil" is the only modern agricultural text-book in which physical chemistry as such has received any recognition.

But on the other hand the physical chemist has not responded to the needs of the agricultural chemist by studying the class of problems with which the latter has to deal. A theory which applies only to very dilute solutions, of few components, and does not consider what part the solvent itself may have in determining the character of the solution products, is of too limited application to be very helpful to the man confronted with practical problems. A more thorough knowledge of irreversible reactions and of thermo-chemistry is as much needed as

a comprehensive solution theory. It is not so important to accumulate evidence in support of our hypotheses as it is to meet the difficulties for which the hypotheses can not account, or for which we have no working hypotheses. Though it may be obviously wrong to expect the student of pure chemistry to devote his attention to problems of applied chemistry, it is not too much to expect him to furnish the methods for attacking these problems, and physical chemistry has yet much to furnish in this direction before it can claim a large support from agriculture on utilitarian grounds.

It is true that the problems presented by agricultural chemistry do not commend themselves to the investigator who is interested in chemistry for its own sake. They are generally complex and not well suited to the elucidation or illustration of hypotheses in pure chemistry. The pecuniary rewards which agricultural chemistry offers are not sufficient in comparison with other fields to tempt the man trained in physical chemistry who wishes to use his equipment to this end. But to the man who has the training and who cares not so much whether his problems be pure science so long as they be attacked in a scientific spirit and with scientific methods, the application of physical chemistry to agriculture offers many opportunities. He can have the satisfaction not only of doing good scientific work, but of helping directly an industry of ultimate importance to all his race and of immediate importance to the numerically largest class of the race.

## NEW BOOKS

**Gesammelte Abhandlungen.** By Robert Bunsen. Herausgegeben von Wilhelm Ostwald und Max Bodenstein. 16 × 24 cm. Erster Band: cxxvi + 535 pp. Zweiter Band: vi + 660 pp. Dritter Band: vi + 637 pp. Leipzig: Wilhelm Engelmann, 1904. Price: paper, 50; bound, 54 marks. — The publication of these three volumes was undertaken by the Bunsen Society, with Ostwald and Bodländer as editors. Everything has been included which was published as a paper under Bunsen's name. This excludes the work of Norton and Hillebrand on cerium, and that of Matthiessen on the electrolytic preparation of the metal of the alkalis and the alkaline earths. Bunsen was one of the great figures in chemistry, and this edition of his works should be studied carefully by every chemist.

The first volume contains, as introduction, memorial addresses by Roscoe, Rathke, and Ostwald; also the speech in which Ostwald urged the German Electrochemical Society to change its name to German Bunsen Society. The papers by Bunsen in this volume include those on arsenic and arsenic compounds; on blast-furnace gases; on the Bunsen cell; and on the electrolysis of fused salts. The second volume is filled with papers arising out of Bunsen's visit to Iceland and with work on gas analysis and the temperature of the flame. In volume three we find the photochemical papers; the first description of the Bunsen burner; the blow-pipe tests; the whole series of papers on spectroscopic analysis, including the discovery of caesium and rubidium; the descriptions of the water pump, the ice calorimeter and the steam calorimeter; the methods of water analysis; and the observations on the condensation of carbon dioxide on glass surfaces.

Ostwald says of Bunsen, that next to Liebig, he was the most successful teacher of chemistry that the world has ever known. The names of Kolbe, Frankland, Landolt, Tyndall, Lothar Meyer, Pebal, Roscoe, Horstmann, Beilstein, Lieben, v. Baeyer, and V. Meyer, show the class of men who worked in the laboratory. In regard to this, Roscoe says: "So from Bunsen all who had eyes to see and ears to hear might learn the important lesson that to found, or to carry on successfully, a school of chemistry the professor must work with, and alongside of, the pupil, and that for him to delegate that duty to an assistant, however able, is a grave error." Although these words were spoken in 1900, Roscoe was referring explicitly to the time before 1876. Ostwald is even more frank and admits that the quality of the students fell off in the last years. Ostwald attributes this to a growing disinclination on the part of Bunsen to devote the same energy to the students. While this may be the case, it seems probable that two other factors are to be considered. The first is that the investigations carried on after 1866 were distinctly less interesting and less important than those done before this date. The second is that with the development of organic chemistry, Bunsen ceased more and more to be a leader. A new branch of science had grown up about which he cared little. When we

reflect that organic chemistry has held for years the place of honor in universities all over the world, it is easy to see that Bunsen might have seemed to many a magnificent survival from a past that was gone to return no more. Fortunately Bunsen lived long enough to see the beginnings of a new period. He was essentially a physical chemist; physical chemistry is slowly but surely relegating the orthodox organic chemistry to a minor position; and it is to a society of physical chemists that we owe this splendid edition of Bunsen's works.

Wilder D. Bancroft

**Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre. By H. W. Bakhuis Roozeboom. Zweites Heft: Systeme aus zwei Komponenten. Erster Teil.** 14 × 22 cm; pp. xii + 465. Braunschweig: Friedrich Vieweg und Sohn, 1904. — This second number contains the first part of the heterogeneous equilibria in binary systems. It gives a complete outline of the equilibria between solid, liquid and gaseous phases for those binary mixtures in which only the components or allotropic forms of the same appear as solid phases.

"The inter-relation of all these equilibria is brought out in a solid figure of my own invention, in which I have taken temperature, pressure, and the concentration of the mixture as the coordinates. This can serve as the type of the large variety of binary mixtures which have been or may be studied. The special form which characterizes the equilibrium relations of each particular system is dependent on the relative volatility and fusibility of the components."

The main sections of the volume are: equilibrium between a liquid and a gaseous phase; representation in space of equilibria; melting and freezing phenomena under atmospheric pressure; the same under varying pressures; polymorphism. Of special interest is the chapter on methods for determining cooling curves and the nature of the solid phases. The methods for determining the composition of solid phases are grouped under the headings: removal and analysis; micrographic methods; conductivity; electromotive force; heats of formation; other methods. This is followed by seventy pages of applications.

There is an enormous amount of material in the book and it is very well arranged. There is only one point that is open to criticism. The author has included the qualitative and quantitative relations. At first sight this seems an admirable plan. While the qualitative relations are exact, the quantitative relations in many cases are but first approximations. When these two sets of relations are interwoven there is danger of the student failing to distinguish between what is permanent and what is ephemeral. The treatment, adopted by the author, makes the book appeal to a larger audience than would otherwise be the case and frees it from the charge of a one-sided treatment. These are real advantages, and it is by no means certain that they have been bought too dearly.

A case of special interest is that of methyl salicylate and camphor. Under a pressure of 21 cm, a solution saturated with respect to camphor contains relatively less camphor than does the vapor. When such a solution is distilled, either the solid or the liquid phase may disappear first, depending on the relative amounts of each. This same phenomenon is also possible with potassium

nitrate and water, but the limiting concentrations are so small as to make the experimental confirmation very difficult.

Wilder D. Bancroft

**Electro-Chemistry. Part I. General Theory.** By R. A. Lehfeldt. Including a Chapter on the Relation of Chemical Constitution to Conductivity. By T. S. Moore. 12 X 18 cm; pp. viii + 268. New York: Longmans, Green and Co., 1904. Price: bound, \$1.60. — The volume deals with the general theory of electrochemistry, the first chapter giving the relation between quantity of electricity and quantity of chemical action, while the third (and last) chapter gives the relation between electromotive force and intensity of chemical action. Between these two is inserted a chapter by T. S. Moore on the relation of chemical constitution and conductivity.

The sections in the first chapter are: Faraday's Laws; mechanism of electrolysis; phenomena at the electrodes; migration of ions; conductivity of electrolytes; equivalent and ionic conductivities; Arrhenius's theory of dissociation; the law of dilution; conductivity of mixtures; non-aqueous solutions; conduction of fused salts. In the third chapter the sections are: voltaic and electrolytic cells; electromotive force; electrode potential; influence of concentration; concentration polarization; chemical polarization; thermodynamic theory; methods of measurement.

On p. 29 the theory offered for the persulphate formation ignores the fact that the maximum yield is obtained in neutral instead of acid solutions. The behavior of nickel as anode in caustic potash solutions, p. 30, is due quite as much to the nickel becoming passive as to the high concentration of hydroxyl as ion. On p. 31 a typographical error makes the equation for hypochlorous acid quite mysterious. On p. 153 the author defines electromotive force as the work done per unit quantity of electricity flowing through the cell. Numerically this is true, but the unsuitableness of it appears when the author writes:

$$\text{volt} = \frac{\text{Joule}}{\text{coulomb}}$$

This is not a definition as is seen if we write it as follows:

$$\text{volt} = \frac{\text{volt} \times \text{coulomb}}{\text{coulomb}}$$

On p. 146 there is also the statement that electromotive force and potential difference are synonymous. This is the more surprising because, on p. 44, the author distinguishes sharply between conductance and conductivity.

It is a pleasure to find numerical data, p. 31, for the relative amounts of chlorine and oxygen given off in the electrolysis of hydrochloric acid. On p. 155 attention is called to the fact, too often overlooked, that Kelvin's deduction of the relation between electromotive force and heat effect was based on the explicit assumption that there should be no heat effect inside the cell except the Joule heat. On p. 228 the possible error in using a voltmeter is brought out much more clearly than is usually the case. This is important because some of the German instruments have such low resistances that they are quite unsuited for measuring potential differences in electrolytic circuits. The discussion of the flowing electrode, pp. 194–201, is good and the author comes to the very sane conclusion "that the question of absolute potentials is at

present only approximately settled." He quotes the recent work of Palmer, which tends to make the potential difference of the decinormal calomel electrode 0.572 volt instead of 0.616 volt, but does not mention the results of Bilitzer.

The conclusions in regard to the deviations from the simple laws of dilute solutions, p. 219, are worth quoting in full:—

"(a) For great dilution (say millinormal and under) the solutions of electrolytes may be regarded as completely ionized, and as giving osmotic pressure (with change of freezing- and boiling-point) and electromotive force in accordance with the simple law of gases, and the conductivity calculated on the same assumptions together with the rule that the mobility of the ions is independent of their concentration.

"(b) For somewhat greater concentrations the degree of ionization must not be regarded as complete, but must be calculated by the law of mass action in the form of Ostwald's rule, otherwise the laws of dilute solutions still hold.

"(c) For the next stage of concentration (deci- to centi-normal in the case of KCl, HCl, etc.), the law of mass action must be applied in the more complex form indicated by the new theory of Jahn and Nernst; hence the logarithmic rule for electromotive force must be given up (as regards strong electrolytes); further, it is probable that the mobility of the ions is sensibly affected by concentration, in which case the conductivity is no longer an exact measure of degree of ionization. The osmotic pressure, however, probably still follows the laws of gases approximately.

"(d) Finally, for strong solutions even the last statement no longer holds. The osmotic pressure may still be calculated from the electromotive force, but there is no safe guide to the degree of ionization." *Wilder D. Bancroft*

**Die Galvanoplastik.** By W. Pfannhauser. (*Monographien über angewandte Elektrochemie. XI. Band.*) 17 × 24 cm; pp. xi + 137. Halle: Wilhelm Knapp, 1904. Price: paper, 4 marks.—The author discusses methods of preparation, plating baths, formation of thick deposits, anodes, apparatus, and special processes. Besides the information which is purely useful, there is a great deal that is also suggestive. The different behavior of ammonium and sodium salts in nickel baths, p. 43, is interesting even though one would like a little more proof in regard to the formation of a nickel ammonium alloy. The precipitation of flexible nickel from hot acid solution, p. 49, needs explanation. Under iron, p. 67, we find the statement made very clearly that the difficulty in depositing nickel on nickel or iron on iron is due to the formation of a surface film. The formation of bright deposits, p. 87, in presence of emulsions is a phenomenon which calls for explanation. The fact, p. 106, that lead cannot be cast direct upon copper suggests relations between the strength of castings and the adherence of plating deposits. The reviewer was much interested in the following paragraph, p. 73, because he had reached a similar point of view independently though subsequently.

"It is not to be denied that there is a certain analogy between the electrolytic precipitation of metals and the crystallization of salts. The change from liquid to solid always occurs with formation of crystals, and larger and more handsome crystals are obtained from solutions the slower the crystallization



takes place. The comparison between the formation of crystals and electrolytic deposits is therefore justified in this point because one can detect a perceptibly crystalline structure when the metal has been precipitated with a very low current density at the cathode. Under the microscope the fracture is seen to have a finer grain the higher the current density used, in other words, the more sudden the change from the state of ions to that of metal." *Wilder D. Bancroft*

**Carborundum.** By Francis A. J. Fitz-Gerald. *Ins Deutsche übertragen von Max Huth. (Monographien über angewandte Elektrochemie. XIII. Band.)* 16 X 24 cm; pp. 44. Halle: Wilhelm Knapp, 1904. Price: paper, 2 marks. — A historical introduction is followed by a chapter on the Acheson carborundum furnace. Then comes a chapter on purification, properties and analysis of carborundum, one on the applications of carborundum, and a final one in which Dorsemagén's proposal to make zinc and carborundum simultaneously is criticized. The use of salt in the charge is thought to be advantageous in carrying off iron. If the salt is really advantageous, it seems more probable that its function is the same as that of the sawdust, to make the mass more porous. The reviewer would have welcomed a diagram showing the voltage and current changes for some furnace during an actual thirty-six hour run. This might well be inserted in the English Edition. It is interesting to notice the detection of adulterations by floating up the carborundum from the corundum by means of a solution of methylene iodide in benzene.

*Wilder D. Bancroft*

**Ready Reference Tables.** By Carl Hering. Vol. I: *Conversion Factors.* 10 X 17 cm; pp. xviii + 196. New York: John Wiley and Sons, 1904. Price: bound, \$2.50. — In a previous notice of this book (8, 510) it was stated that reference was made only to the legal volt. This was an error as the following quotation shows. "The value adopted at the Reichsanstalt for the electromotive force of the Clark cell is based upon a determination of its E. M. F. in terms of the electrochemical equivalent of silver and the unit of resistance, and also upon a similar determination of the E. M. F. of the Weston or cadmium cell, together with a determination of the ratio of the values of these two cells. As the values thus obtained for the Clark and Weston or cadmium cells by the silver voltmeter did not agree with the directly determined ratio, each of the silver voltmeter determinations was given equal weight and the two separate values adjusted so as to give the ratio directly determined. The Reichsanstalt's value thus obtained for the Clark cell is 1.43285 instead of 1.434 as defined by the International Congress, and legal in this country. This Reichsanstalt value may be more accurate, but is not legalized here. As the cells are the same, this makes a very slight difference between the volt used by the Reichsanstalt and that legal and used in this country (the international volt). The National Bureau of Standards uses as the fundamental units those of resistance and electromotive force, obtaining the ampere from them, thus bringing all three into agreement with each other. According to Weston the international concrete volt, ampere, and ohm, as defined by the Chicago Congress, agree with each other."

*Wilder D. Bancroft*

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